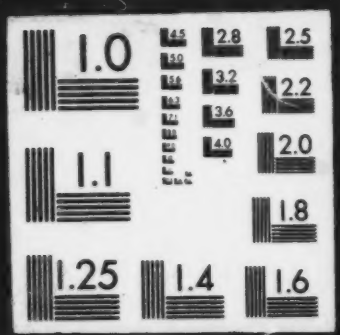
1 OF 1
PB
215659



PB-215 659

INVESTIGATION OF PHOTOCHEMICAL REACTIVITIES OF ORGANIC SOLVENTS

K. W. Wilson, et al

Stanford Research Institute
Irvine, California

September 1970

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 215 659

Final Report

INVESTIGATION OF PHOTOCHEMICAL REACTIVITIES OF ORGANIC SOLVENTS

Prepared for:

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
CINCINNATI, OHIO

Contract No. CPA 22-69-125

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

STANFORD RESEARCH INSTITUTE
SRI-Irvine · Irvine, California 92664 · U.S.A.

81

STANFORD RESEARCH INSTITUTE
SRI Irvine · Irvine, California 92664 · U S A

Final Report

September 1970

INVESTIGATION OF PHOTOCHEMICAL REACTIVITIES OF ORGANIC SOLVENTS

Prepared for:

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
CINCINNATI, OHIO

Contract No. CPA 22-69-125

Attention: S. L. Kopczynski

By: K. W. Wilson
G. J. Doyle

Details of illustrations in this document may be better studied on microfiche.

SRI Project PSU-8029

E. C. Wood

Approved:

E. C. Wood
Executive Director
SRI-Irvine

CONTENTS

I	INTRODUCTION	1
II	SUMMARY AND CONCLUSIONS	3
III	RESULTS AND DISCUSSION	6
	Test Solvent in Nitrogen Dioxide (Group I Experiments)	6
	Test Solvent in Photoreactive Mixture (Group II Experiments)	8
IV	STRUCTURE, REACTIVITY, AND REACTION MECHANISMS	13
V	EXPERIMENTAL METHODS	18
ACKNOWLEDGEMENTS		22
REFERENCES		23
ILLUSTRATIONS		25
TABLES		38
APPENDIX		
A	DESIGN AND PERFORMANCE OF A FACILITY (SMOG CHAMBER) FOR STUDYING PHOTOCHEMICAL REACTIONS UNDER CONDITIONS SIMULATING THE TROPOSPHERIC ATMOSPHERE	A-1

ILLUSTRATIONS

1	Rankings Based on Normalized Maximum Oxidant	26
2	Rankings Based on Solvent Reaction Rate	27
3	Rankings Based on Nitrogen Dioxide Dosages in Runs with Background Mix Plus 8 ppm Test Solvent	28
4	Rankings Based on Nitrogen Dioxide Dosages in Runs with Background Mixes Plus 4 ppm Test Solvent	29
5	Rankings Based on Nitrogen Dioxide Half-Lives in Runs with Background Mix Plus 8 ppm Test Solvent	30
6	Rankings Based on Nitrogen Dioxide Half-Lives in Runs with Background Mixes Plus 4 ppm Test Solvent	31
7	Rankings Based on Oxidant Maxima in Runs with Background Mix Plus 8 ppm Test Solvent	32
8	Rankings Based on Oxidant Maxima in Runs with Background Mixes Plus 4 ppm Test Solvent	33
9	Rankings Based on Oxidant Dosages in Runs with Background Mix Plus 8 ppm Test Solvent	34
10	Rankings Based on Oxidant Dosages in Runs with Background Mixes Plus 4 ppm Test Solvent	35
11	Predicted Versus Calculated Rates of Disappearance of Test Solvents	36
12	Predicted Versus Calculated Increase in Maximum Ozone	37

APPENDIX ILLUSTRATIONS

1	Air Purification System for SRI Smog Chamber	A-5
2	Equilibrium Concentrations of Nitrogen Oxides in Air at 8 atm and Varying Temperatures	A-8

Illustrations (Concluded)

Appendix Illustrations (concluded)

3	Schematic Diagram of Airflow Control and Mixing System of SRI Smog Chamber	A-11
4	Isometric Sketch Showing Size and Shape of SRI Smog Chamber. . .	A-13
5	Estimated and Measured Irradiance from Sun Plus Sky.	A-15
6	Spectral Power Distributions of Various Fluorescent Lamps. . . .	A-19
7	Cross-Section of Eye Port.	A-22
8	Static Run with Initial Concentrations of 1.0 ppm Nitric Oxide and 8 ppm Ethylene in SRI Smog Chamber	A-27

TABLES

1	Irradiation Experiments with Test Solvents and Nitrogen Oxides	39
2	Irradiation Experiments with Standard Background Mixes and Ketone and Alcohol Solvents	40
3	Irradiation Experiments with Standard Background Mixes and Ester and Ether Solvents	41
4	Irradiation Experiments with Standard Background Mixes and Miscellaneous Solvents	42
5	Effect of Solvent Concentration on Background Mix	43
6	Effect of Solvent (4 ppm) on Different Background Mixes	44
7	Solvent Reactivity Category Summary	45
8	Weakest Bonds in Test Solvents	46

APPENDIX TABLES

1	Equilibrium Constants Used to Calculate Nitrogen Oxide Concentrations at 8 Atmospheres	A-9
2	Initial and Final Lamp Mixes	A-20
3	Estimates of Integrals of Irradiance 300-450 nm in Chamber with Flat White Reflector and with First Approximation to Lamp Mix	A-25

I INTRODUCTION

An appreciable amount of research has been completed on the photochemical reactivities of hydrocarbons associated with automobile exhaust emissions. Some of these hydrocarbons have been investigated by different groups using irradiation chambers of various designs. As a result, five or more different ways have been adopted for measuring quantitatively the photochemical reactivity of a compound; no standard definition of reactivity has yet been adopted by the several groups making these measurements. Much less experimental effort has been directed toward measuring the photochemical reactivities of organic solvents. Some data were obtained as incidental parts of studies dealing primarily with auto exhaust, but reports of studies dealing specifically with solvents are limited. Data that have been published indicate that most solvents react much more slowly than do the reactive hydrocarbons found in auto exhaust.

During the period when irradiation chamber studies sought primarily to elucidate the mechanism of photooxidation of automobile exhaust in the atmosphere, methods for conducting these studies became standardized to a certain extent. These methods gave results that could be extrapolated to the atmosphere for many localities where automobile exhaust is a major source of air pollution. The presence of pollutants from other sources influences the reactions of auto exhaust to some degree, but does not make any radical changes in the course of the reaction.

Traditionally auto exhaust reactivity has been measured in smog chambers by irradiating air containing trace concentrations of exhaust. The ratio of hydrocarbon to nitric oxide has been varied by changing operating parameters of the car or by adding pure chemicals to the smog chamber. The general method--the irradiation of air containing traces of solvent and nitric oxide--used so far for measuring reactivities of solvents (slow reactors) is the same as that used for measuring the reactivity of auto exhaust (a much faster reactor). Consideration of conditions prevailing in the atmosphere leads to the conclusion that these methods are not realistic for solvent studies. Solvents are usually vaporized into the atmosphere at low temperatures. The oxides of nitrogen required for their photooxidation must come from other sources--for example, from automobile exhaust. Thus, in the atmosphere an organic solvent reacts in an environment where fast reactors (from automobile exhaust) are also present. It has been demonstrated in several instances that the presence of these fast reactors accelerates the rates of disappearance of slow reactors.

In the study reported herein, we have evaluated the reactivities of 20 organic solvents by traditional methods and by modified methods in which a

background mix was added as a first step toward simulating an urban atmosphere containing reacting auto exhaust. The relative reactivities of the 20 solvents as measured by the traditional and the modified experimental methods were thus determined. From a comparison of results obtained by both methods, certain conclusions were reached about the mechanism of the photochemical reactions of solvents. For the systems studied, a reasonable mechanism was proposed. However, because the work was a broad survey of many solvents, the composition of the background mix was chosen somewhat arbitrarily, as were the concentrations of all reactants. Additional experimental programs would have to be undertaken to determine whether our conclusions are applicable to other background mixtures and concentration levels.

II SUMMARY AND CONCLUSIONS

The photochemical reactivities of the following 20 commercial solvents were measured by experiments using a smog chamber: methyl isobutyl ketone, methyl isoamyl ketone, methyl ethyl ketone, cyclohexanone, diacetone alcohol, isopropyl alcohol, isobutyl alcohol, n-butyl alcohol, n-butyl acetate, isobutyl acetate, sec. butyl acetate, ethyl acetate, diethyl cellosolve, cellosolve acetate, toluene, n-nonane, 2-nitropropane, 1,1,2-trichloroethane, methylene chloride, and Freon 113. All solvents tested are said to be widely used commercially or are being considered as substitutes for commercial solvents (particularly methyl isobutyl ketone) whose use is restricted by certain air pollution control agencies. Each solvent was studied in a simple system comprising pure air, nitrogen dioxide, and the individual test solvent (Group I experiments) and in a more complex mixture comprising pure air, propylene, toluene, butane, and nitrogen dioxide (Group II experiments) and the test solvent. To the extent possible, the test solvents were selected to give groups of chemicals that differed systematically in certain structural features so that conclusions could be drawn relating structure and reactivity. Reactivities were evaluated by measuring dosages* of nitrogen dioxide, oxidant, ozone, and PAN (peroxyacetyl nitrate); rates of disappearance of nitrogen dioxide, test solvent, propylene, toluene, and butane; eye irritation level; and maximum aerosol level. Some of these measurements varied sufficiently so that they could be used as criteria for ranking the solvents.

Nitrogen dioxide dosages were influenced very little by the nature of the solvent in the Group I experiments. The single exception was toluene, which gave a significant decrease in nitrogen dioxide dosage. In the Group II experiments, the nitrogen dioxide half-life and dosage of the background mix were always decreased by the addition of toluene and diethyl cellosolve and increased by the addition of cyclohexanone. For the remainder of the test solvents, the effects on the background mix were less marked and the rankings depended somewhat on the concentrations of test solvent and nitrogen dioxide.

Oxidant maxima and dosages provide the most convenient criteria for ranking the solvents because the spread in values was large compared to the experimental uncertainties in the measurements. Diethyl cellosolve and cellosolve acetate consistently gave the highest oxidant readings--well above background levels--in Group I and II experiments. In Group II experiments, toluene reduced the oxidant level of the background mix while Freon 113, methylene chloride, 1,1,2-trichloroethane, cyclohexanone, and methyl ethyl ketone had little effect. The remainder of the test solvents, when added to the background mix, increased the oxidant maxima, with esters producing

---

* The area under the concentration vs time curve.

the greatest increase and ketones the least. Generally more than 85% of the total oxidant was ozone, except in Group II experiments with diethyl cellosolve where only 71% of the total oxidant was ozone.

Eye irritation was not detected in any of the Group I experiments. In the Group II experiments the propylene in the background mix produced most of the eye irritants; any additional irritants formed from the test solvents were present in amounts too small to be detected.

Aerosol formation was insignificant in all Group I experiments. In Group II experiments, it was observed for toluene at the 4 and 8 ppm levels and for cyclohexanone at the 8 ppm level; none of the other solvents gave aerosol that was significantly different from that observed for the background.

Rates of disappearance of test solvents varied slightly from solvent to solvent in the Group I experiments, with diethyl cellosolve and cellosolve acetate reacting the fastest. In the Group II experiments, the rates of disappearance of butane and toluene were unaffected by the addition of test solvents. The rate of disappearance of propylene was increased slightly by the addition of diethyl cellosolve, was decreased slightly by the addition of cyclohexanone, and was unchanged by the addition of all other test solvents.

Present knowledge about the photochemical reaction mechanism is insufficient to explain all results; however, some speculation is possible--particularly on the results of Group II experiments. In these, the rates of disappearance of the test solvents varied in a manner consistent with the concept that carbon-hydrogen bonds in the solvent are attacked by some reactive intermediate produced by irradiation of the background mixture. The weighting factors for rates of abstraction of primary, secondary, and tertiary hydrogens were found to be 0.11, 0.21, and 0.40, respectively, suggesting that some nonselective radical--possibly hydroxyl--is the attacking species. The effect of the solvent on maximum ozone (or oxidant) concentration is more difficult to explain because ozone results from a complicated series of reactions. Analysis of Group II data suggests that abstraction of primary hydrogens enhances ozone formation while abstraction of secondary hydrogens has a minor effect and abstraction of tertiary hydrogens actually suppresses ozone formation. So little is known about the mechanism of nitrogen dioxide disappearance that no satisfactory explanation could be devised for our results.

The most important implication of this treatment of the experimental data is that reactivity of saturated compounds in a matrix simulating an atmosphere polluted with auto exhaust is governed more by the types and numbers of carbon-hydrogen bonds in the molecule than by the presence or absence of oxygenated functional groups. The results suggest that photochemical reactivities of saturated compounds in a reacting background mixture might

be predicted on the basis of a relatively simple model. The determination of the rates of reaction of hydroxyl with hydrogen atoms in a carefully selected series of compounds could provide information of great value in determining whether hydroxyl is the important reactive intermediate.

III RESULTS AND DISCUSSION

Photochemical reactivity has been defined[1] as:

> . . . the tendency of an atmospheric system containing organic substances and nitrogen oxides to undergo, under the influence of ultraviolet radiation and appropriate meteorological conditions, a series of chemical reactions that results in the various manifestations associated with the photochemical type of air pollution.

The photochemical reactivity of an atmospheric system depends on the concentrations and concentration ratios of the reactants as well as their chemical structures. Most experimental measurements of reactivity have been made* by irradiation of mixtures containing single organic compounds and nitrogen oxides; the assumption is frequently made that additivity of reactivities occurs in complex mixtures. Theoretical considerations and recent experimental data indicate that the assumption of additivity of effects is unjustified in many cases.[3-6]

In the work reported herein, the photochemical reactivities of 20 commercial solvents were measured by irradiation of mixtures containing single organic compounds and nitrogen oxides (Group I experiments) and by irradiation of each of the 20 solvents in a simple mixture containing the solvent, butane, toluene, propylene, and nitrogen dioxide (Group II experiments). The results of these experiments then were used to formulate various reactivity ratings for these solvents.† In Section IV we discuss the relationship between chemical structure and reactivity and speculate on reaction mechanisms.

Test Solvent in Nitrogen Dioxide (Group I Experiments)

The chamber was initially charged with 1 ppm of test solvent and 0.1 ppm of nitrogen oxides. The results of these irradiation experiments are given in Table 1.‡ No values for PAN are given because, when present, its concentration was near the limit of detectability (0.05 ppm). The initial concentrations of nitrogen oxides (Table 1) were not identical for each experiment because the air purification system used with the smog chamber was sometimes unable to reduce the nitrogen oxides concentration to the 0.10 ppm level. However, the effects on reactivity of varying initial concentrations of nitrogen oxides are predictable and were taken into account in interpreting

---

* For a convenient summary, see Reference 2.

† Experimental procedures are described in Section V.

‡ All tables and figures are at end of text.

the results. The differences and trends shown by the data in Table 1 are summarized in the following paragraphs.

Nitrogen dioxide dosage was primarily a reflection of the concentrations of nitrogen oxides present in the initial chamber charge and was influenced little, if any, by the chemical structure of the test solvent. The single exception was toluene, which clearly reduced the nitrogen dioxide dosage and therefore was more reactive than the other solvents.

Oxidant values reported in Table 1 (which are corrected for the nitrogen dioxide contribution) were almost identical with the ozone values, indicating that the oxidant was primarily ozone. Possible exceptions are the experiments with diethyl cellosolve, where the oxidant values were slightly higher than the ozone values, indicating that some other oxidant--possibly a hydroperoxide--may have been present. Maximum oxidant levels are related in some way to the levels of nitrogen oxides in the initial chamber charge which, as explained earlier, were difficult to maintain constant. As a crude attempt to correct for these differences, we assumed that the maximum oxidant level was directly proportional to the maximum nitrogen dioxide level; therefore, all oxidant maxima were normalized to 0.10 ppm maximum nitrogen dioxide. Figure 1 presents a ranking of the test solvents according to the normalized maximum oxidant levels. Almost all solvents caused an increase in oxidant above background levels; however, at these relatively low concentrations of nitrogen oxides and oxidant, the experimental uncertainties make a precise ranking difficult.

Rates of disappearance* were small, but measurable, for most of the solvents. Figure 2 presents a ranking of the test solvents according to rate of disappearance. Diethyl cellosolve reacted fastest, with n-butyl alcohol, cellosolve acetate, and n-nonane reacting almost as rapidly; even diethyl cellosolve reacted an order of magnitude slower than a reactive olefin in a similar environment.

Eye irritation indices for test solvent experiments were compared with indices for irradiated pure air by using the Student t test.† Values of t and the number of degrees of freedom also are listed in Table 1. A value of t of 1.9 or greater indicates irritation different (at the 90% confidence level) from irritation found with pure air. All values of t are well below this value, indicating that no significant eye irritation was found in any of

---

* The solvent reaction rates reported in Table 1 have not been corrected for chamber leakage rate. This varied somewhat but was generally in the range of 3% ± 2% per hour.

† See pages 20 and 21 for a discussion of methods of evaluating eye irritation data and the justification for our selection.

these experiments. If many more replications were run, significant differences perhaps would be revealed. On the basis of our experiments, none of the solvents is reactive as judged by production of eye irritants.

Aerosol values in all experiments were below those normally measured for clean ambient air. Typical ambient light scattering values range from 3 (on a clear day) to 15 or 20 (on a smoggy day). Many of the maximum aerosol values observed in our experiments coincided with the times that the eye panel was exposed. We believe that the readings were caused by the introduction into the chamber of face powder, eye makeup, or other contaminant during the exposure periods. None of the solvents would be classed as reactive on the basis of aerosol formation in a Group I experiment.

Using a reactivity rating scheme similar to that proposed by Altshuller,[7] in which reactivity is based on the ability of the test compound to form ozone or oxidant, PAN, aerosol, and eye irritants (we have no data on formaldehyde or plant damaging compounds), we would conclude that oxidant formation is the only criterion suitable for judging the reactivity of solvents from the data obtained in Group I experiments. None of the solvents form PAN, aerosol, or eye irritants in sufficient quantity to be classified as reactive by these criteria. Figure 1, therefore, represents the ranking of these test solvents according to a conventional scheme.

Test Solvent in Photoreactive Mixture (Group II Experiments)

The background mixture chosen to simulate auto exhaust contained propylene (to represent the olefinic components), toluene (to represent the aromatic components), and butane (to represent the saturated components); the concentrations of these hydrocarbons were 0.5, 1.0, and 2.0 ppm, respectively. Either 1.0 or 0.5 ppm of nitrogen dioxide and 8 or 4 ppm of test solvent were added to the background mixture. The results of the experiments with ketones and alcohols are given in Table 2, those with esters and ethers are given in Table 3, and those with the remaining test solvents are given in Table 4. For this type of experiment, the reactivity of a test solvent must be judged by the extent to which it perturbs the reactivity of the background mix. The trends and differences shown by the data in these tables are summarized in the following paragraphs.

The nitrogen dioxide dosage during 7 hours of irradiation was used as one means of ranking the test solvents. These rankings are shown in Figures 3 and 4. Cyclohexanone, when added to the background mix, increased the nitrogen oxides dosage in all experiments. Diethyl cellosolve and toluene always decreased the dosage. The changes produced by the other solvents were less marked, and the rankings depended somewhat on the concentrations of test solvent and nitrogen dioxide. No clearcut trends within classes of similar compounds were evident. Rankings according to nitrogen dioxide half-lives are shown in Figures 5 and 6. For the experiments with 8 ppm of test solvent

(Figure 5), the rankings are approximately the same based on half-lives or dosages. Rankings based on experimental data using 4 ppm of test solvent (Figure 6) are less consistent, but still show that diethyl cellosolve and toluene always decreased the half-life and cyclohexanone increased the half-life.

Oxidant values (those in the tables are corrected for nitrogen dioxide contribution) were always about 10% higher than ozone values for the background mix alone and for the experiments with ketones, alcohols, esters, and all miscellaneous solvents except toluene. In experiments with toluene, almost all of the oxidant was ozone. Cellosolve acetate gave oxidant values 15% to 20% higher than ozone values, and diethyl cellosolve gave oxidant values 20% to 25% higher than ozone values. This difference was not an experimental artifact and indicates that some oxidant other than ozone was present. The identification of this non-ozone oxidant was beyond the scope of this research; however, we speculate that it was a hydroperoxide.

Test solvent rankings on the basis of oxidant maxima observed in these experiments are given in Figures 7 and 8. Toluene always reduced the oxidant maximum of the background mix while diethyl cellosolve and cellosolve acetate always produced marked increases in oxidant maxima when added to the background mix. Freon 113, methylene chloride, 1,1,2-trichloroethane, cyclohexanone, ethyl acetate, and methyl ethyl ketone had little effect on the oxidant produced by the background mixes. The remainder of the test solvents, when added to the background mix, increased the oxidant maxima, with esters producing the greatest increase and ketones the least. In Section IV of this report these results are analyzed further, leading to the conclusion that the numbers of primary, secondary, and tertiary hydrogen atoms in the solvent molecule (rather than the functional groups) determine the effect on oxidant maxima.

Rankings according to oxidant dosages are shown in Figures 9 and 10. In general, the results are similar to the rankings based on oxidant maxima, and no further comment seems to be required.

PAN formation from the background mix was not influenced significantly by the addition of any of the test solvents. All measured concentrations of PAN were small and fairly close to the limit of detectability for our method; therefore, small changes in concentration could not be measured.

Rates of disappearance of butane and toluene from the reaction mixture were unchanged by the addition of any of the test solvents to the background mix. The rate of disappearance of propylene was also unchanging except in the experiments with cyclohexanone where the rate was decreased slightly and in the experiments with diethyl cellosolve where the rate was increased slightly.

Rates of disappearance of all test solvents except Freon 113 were greater than the chamber leakage rate. No strong trends related to type of compound were evident; the rate was more a function of the number and nature of carbon hydrogen bonds in the molecules. The results are discussed in detail in Section IV.

Eye irritation indices of the background mix with and without the addition of test solvent were compared using the Student t test.* Values of the t and df (degrees of freedom) are given in Tables 2-4. Significant differences at the 90% confidence level are indicated by t values between 1.78 (for 12 df) and 2.02 (for 5 df). The test indicates that cyclohexanone at the 4 ppm level caused an increase in the irritation produced by Background Mix 2. Cyclohexanone at the 8 ppm or 4 ppm level did not change the irritation produced by Background Mix 1. More repetitions should be run to confirm this conclusion--particularly because the t value does not indicate a difference at the 95% confidence level. No other solvents caused significant changes in the irritation produced by the background mix.

Aerosol above background level was found in the experiments with 8 ppm of cyclohexanone and 4 and 8 ppm of toluene but not in any of the other experiments. In the experiments with toluene, the amount of aerosol was significantly decreased by reducing the concentration of nitrogen dioxide in the background mix. To the best of our knowledge, the effect on aerosol production of the hydrocarbon:nitrogen oxides ratio has not been studied and deserves further evaluation. This may be an extremely important factor in predicting visibility reduction accompanying photochemical smog formation.

Data from the two series of runs--one with 8 ppm of solvent and Background Mix 1 and the other with 4 ppm of solvent and the same background mix--should serve as a starting point for predicting the effect of smaller, more realistic concentrations of solvent. Pertinent experimental results are summarized in Table 5. One would expect that the effects produced by the solvent would decrease as the solvent concentration is decreased, and at some minimum concentration--different for each test solvent--the results would become indistinguishable from those observed with the background mix alone. Results with 4 ppm of test solvent are closer to the background mix than results with 8 ppm of test solvent (except for 4 ppm of isobutyl alcohol which looks anomalous). In some instances, 8 ppm of test solvent produced twice the change caused by 4 ppm; however, in most cases there was definitely not a linear relationship between the changes in nitrogen dioxide half-lives or dosages or oxidant maxima dosages produced by adding the test solvent to the background mix and the concentration of added test solvent. Thus, from the

* See pages 20 and 21 for a discussion of methods of evaluating eye irritation data and the justification for our selection.

data we have, it is impossible to extrapolate and predict the effect of adding smaller concentrations to the background mix. Additional data from runs made with lower concentrations of solvent are required to predict the effects of adding "real life" concentrations of solvents to an urban atmosphere.

Data from the two series of runs--one with 4 ppm of solvent and Background Mix 1 and the other with 4 ppm of solvent and Background Mix 2--should provide a basis for predicting whether the reactivity rankings depend on the nitrogen dioxide concentration in the initial chamber charge. Pertinent data are summarized in Table 6 and rankings have already been set forth in Figures 4, 6, 8, and 10. As expected, the experiments using Background Mix 1 with 1.00 ppm nitrogen dioxide gave larger nitrogen dioxide dosages, oxidant maxima, and oxidant dosages than the experiments using Background Mix 2 with 0.50 ppm nitrogen dioxide. The half-life of nitrogen dioxide did not vary systematically with its concentration. Rankings based on oxidant maxima (Figure 8) and oxidant dosages (Figure 10) are almost identical for the two series of experiments; rankings based on nitrogen dioxide dosages (Figure 4) differ considerably between the two series, but this is caused in large part by the low values and appreciable experimental uncertainties at the low concentration of nitrogen dioxide. As mentioned earlier, lowering the concentration of nitrogen dioxide produced a marked decrease in the aerosol produced from toluene. None of the other test solvents produced aerosol, so it was impossible to say whether this general effect could be expected in all experiments where aerosol is formed.

Reactivity rankings, based on data obtained in experiments involving the test chemical and a background mix have not been standardized. Perhaps a scheme similar to Altshuller's[7] could be used, with the assignment of either positive or negative rating numbers to each chemical as a measure of the increase or decrease in undesirable reaction products (ozone or oxidant, PAN, formaldehyde, aerosol, eye irritants, and plant damaging compounds) produced by addition of the test compound to the background mix. From our experiments we have no data on formaldehyde production or plant damage, and no differences in PAN or eye irritant values were observed, (except for a barely significant increase caused by cyclohexanone); therefore, our reactivity rankings must be made primarily according to differences observed in ozone (or oxidant) production, nitrogen dioxide removal, and aerosol formation. We suggest the following rating scheme.

Reactivity Rating	Nitrogen Dioxide Half-Life, Oxidant Maximum, and Oxidant Dosage	Aerosol
+2 (large increase in undesirable products)	>160% of base mix	>6 units
+1 (moderate increase in undesirable products)	120%-160% of base mix	3-6 units
0 (insignificant effect on undesirable products)	90%-120% of base mix	1-3 units
-1 (moderate decrease in undesirable products)	70%-90% of base mix	Not applicable
-2 (large decrease in undesirable products)	<70% of base mix	Not applicable

Using this scheme we can formulate the category summary given in Table 7. No averaged rating is given because no precedent exists for evaluating test compounds that decrease undesirable smog products. A discussion of interrelationships among structure, reactivity, and reaction mechanisms is given in Section IV.

IV STRUCTURE, REACTIVITY, AND REACTION MECHANISMS

The work performed in this study deals with two groups of experiments: Group I experiments involving an individual test solvent and nitrogen dioxide and Group II experiments involving the test solvent in a photoreactive background mixture. In the Group I experiments, each solvent would react by a mechanism unique to itself; our study was too limited to provide sufficient data to enable us to deduce the mechanism for the reaction of each of the 20 solvents. However, in the Group II experiments, it is likely that the slow reacting solvents perturbed only moderately the concentration of reactive intermediates prevailing in the background mixture, so that the data can be regarded as resulting from exposure of the solvents to reaction with the kinds and concentrations of intermediate characteristic of the background. Consequently, these data offer the best opportunity for comparative analysis.

The first step in a possible chain of reactions involving the test solvent should be the reaction of a solvent molecule with some reactive intermediate from the background mixture. Our best measure of this reaction rate is the rate of disappearance of the test solvent. A scan of the data in Tables 2-4 reveals only a modest four- to eightfold range in the rate of disappearance* of the solvent. This is excepting from consideration toluene (the sole aromatic) and Freon 113 (a molecule without a carbon-hydrogen bond). Such a range would correspond to a range in activation energies of, at most, 1.4 kcal/mole, assuming a nearly constant pre-exponential factor. The most likely mode of attack on these saturated compounds is the abstraction of hydrogen from the weakest carbon-hydrogen bond. The bond dissociation energies for these weakest bonds are listed in Table 8; these vary from 89 to 104 kcal/mole. To account for an observed range in activation energies of 1.4 kcal/mole in reactions involving bonds whose dissociation energies vary over a 15-kcal/mole range, we proposed a nonselective hydrogen abstraction yielding at least one product of high exothermic heat of formation.[8] For reactive intermediates of this type, variation in rate from solvent to solvent would be governed principally by the number and type of carbon-hydrogen bonds and the nature of the activated complex. The range encompassed by the rate of solvent disappearance in the data given here is accounted for more believably by such factors, although there could also be minor variations in the energy of activation. On the basis of these arguments, it was decided to attempt a correlation of rate of disappearance with number and types of carbon-hydrogen bonds.

The data for logarithmic rate of disappearance of the solvents in the presence of simulated exhaust (corrected for chamber leakage) were correlated

---

* Corrected for chamber leakage rate.

by fitting a simple expression

$$R_i^* = AP_i + BS_i + CT_i \ \% \ hr^{-1}$$

where A, B, and C are the coefficients to be determined and P_i, S_i, and T_i are the numbers of primary, secondary, and tertiary hydrogens, respectively, bonded to carbon atoms in the i^{th} compound. The maximum liklihood estimation of A, B, and C resulted in the values 0.11, 0.21, and 0.40, and this fitted the data to a standard deviation of $\pm 0.86\%$ hr^{-1}. Most of the contribution to the deviation was by the two cellosolves and nonane. The fit is illustrated by a plot of R_i (measured rate) versus R_i^* (predicted rate) in Figure 11. The numbers near the points correspond to the numbers of the solvents in Table 8. The maximum likelihood line serves as a convenient reference level for discussing rate of disappearance and possible refinements of the correlation. The correlation suggests that the attacking species should react most rapidly with tertiary hydrogens, less rapidly with secondary hydrogens, and slowest with primary hydrogens. One method of identifying possible reactive intermediates is to determine whether their relative reaction rates with various kinds of hydrogens agree with those determined by our correlation. This is done in the following paragraph for hydroxyl--a possible reactive intermediate.

Fragmentary data on the specific rate at 300°K for reaction of saturated hydrocarbons with hydroxyl radicals are shown in the following tabulation.[9]

Hydrocarbon	Specific Rate ($pphm^{-1}hr^{-1}$)
C_2H_6	266
C_3H_8	1240
iso C_4H_{10}	1860

Treated by the same linear correlation method as above, these data yield

$$k_i^* = 44.3P_i + 487S_i + 1461T_i \ pphm^{-1}hr^{-1}$$

and, comparing the relative weights of the three terms in the two expressions, we see that they are in corresponding order but that there is a large and

possibly fictitious disagreement on the effect of primary hydrogens. Radical abstraction of hydrogens by some species resembling hydroxyl radical is clearly suggested by this comparison.

If the simplifying assumption--that hydroxyl radicals are the only species attacking the solvent molecule at a significant rate--is made, then on this basis an upper limit for the hydroxyl radical concentration in the mixture should be about 3×10^{-6} pphm averaged over the duration of these experiments. It was obtained by a maximum likelihood procedure applied to the two sets of three coefficients in the two correlative expressions, which yielded a value of $10^{-2}/[OH] = 3210$ pphm^{-1}.

This upper limit agrees with an upper limit that can be estimated from Bureau of Mines data* on the rate of disappearance of carbon monoxide in a photooxidizing background mixture of air containing trace concentrations of 1-butene and nitric oxide. In this work, the rate of conversion of carbon monoxide to carbon dioxide was observed to be 0.1% hr^{-1}. Published estimates[10-13] of the rate constant for the reaction of carbon monoxide and hydroxyl range from 75 to 168 pphm^{-1} hr^{-1}. On the assumption that the carbon monoxide disappears only by the reaction $CO + OH \longrightarrow H + CO_2$, the calculated concentration of OH is found to range from 6×10^{-6} to 13×10^{-6} pphm. This is in excellent agreement with the average value of 3×10^{-6} pphm calculated from the rates of disappearance we found in the Group II experiments.

Using the maximum likelihood line of Figure 11, one can classify the tested solvents on the basis of their deviation from it. Table 8 enumerates the percentage deviation along with the carbon-hydrogen bond dissociation energies of the weakest bonds and the number of such bonds in the molecule. The rate of disappearance of the solvent shows very little correlation with bond energies. Presuming hydroxyl radical attack, this would be expected on the basis of published data[8] as long as the reaction

$$RH + OH \longrightarrow H_2O + R$$

is exothermic by more than about 10 kcal. This imposes the condition that the bond dissociation energy of the carbon-hydrogen bonds be less than 108 kcal. The compound that came closest to not satisfying this condition is methylene chloride and its measured rate of disappearance is essentially zero. Differences in rate probably are due mostly to variations in the entropy of activation for the reaction (Arrhenius A factors). There is little profit in speculating about these variations on the basis of the data, although some progress might be made along the lines described in Reference 8.

* Personal communication.

If the hydroxyl attack hypothesis is later confirmed, then more profitable studies would consist of determining the specific rate constant for the reaction of hydroxyl with the solvents and ranking them according to rate of reaction.

Some indications of the behavior of classes of compounds are contained in Table 8. These are purely tentative because of the large experimental uncertainties in the rates of disappearance. Ketones tend to react slightly slower than average; alcohols tend to react faster. Acetate esters seem a little slow. The cellosolves are definitely faster than average. The other miscellaneous compounds had no homologs in the study to allow tentative conclusions about class behavior.

Toluene was not included in the above correlations because it is a constituent of the background matrix and is an aromatic compound. It reacts at an average rate of 1.7% hr^{-1}, indicating a specific rate with hydroxyl of about 6000 $pphm^{-1}hr^{-1}$ at 300°K. However, the bond dissociation energy of ϕCH_2-H is about 85 kcal, the lowest of all carbon-hydrogen bonds encountered in this study. Thus, for toluene it is likely that appreciable contributions to the observed rate are made by reactive species other than hydroxyl. If estimates of the rates of the reaction between hydroxyl and the other solvents are upper limits, then this value for toluene is even more of an upper limit, and the true value may be orders of magnitude less than the quoted value.

The effect of the solvents on the maximum ozone concentration achieved in the matrix is a less straightforward matter. The ratio

where

$$\frac{[O_3] - [O_3]_o}{[S]}$$

$[O_3]$ = maximum ozone concentration observed with solvent in background mixture

$[O_3]_o$ = the same quantity in the absence of solvent

$[S]$ = initial solvent concentration

was correlated with types and numbers of carbon-hydrogen bonds and gave

$$\frac{[O_3] - [O_3]_o}{[S]} \times 10^2 = 0.199P + 0.055S - 0.209T$$

The degree of correlation offered by this expression is shown in Figure 12, where measured values are plotted against predicted values. This correlation

must be treated with caution because of the undoubtedly complex reaction scheme leading to ozone formation. It does suggest that abstraction of primary hydrogens enhances ozone formation, while abstraction of secondaries has a minor effect and abstraction of tertiaries actually suppresses ozone formation. An attempt at adjustment for rate of abstraction may be carried out by combining this correlation with the correlation of rate of disappearance:

$$\frac{[O_3] - [O_3]_o}{[S]} \times 10^2 = (0.11)(1.86)P + (0.21)(0.26)S + (0.40)(-0.52)T$$

This yields a ratio of 8:1:(-2) for relative effectiveness. However, this should not be taken too seriously until confirmatory work is done. The negative effect of tertiary carbon-hydrogen bonds may be influenced by the fact that such bonds were present only in ketones, alcohols, and acetate esters in this study.

The most important implication of this treatment of the experimental data is that the reactivity (as measured by rate of disappearance) of saturated compounds in a mixture simulating an atmosphere polluted with auto exhaust is governed more by the types and numbers of carbon-hydrogen bonds in the molecule than by the presence or absence of functional groups such as carboxyl or hydroxyl. The work suggests that a relatively simple mechanistic model might be formulated to account for the reactions of saturated compounds in the presence of photooxidizing olefins and nitrogen oxides. The reactive intermediates probably could be characterized with adequate certainty in an experimental program specifically designed for this purpose. Experiments would have to be designed to determine whether aromatics have a unique function in determining the concentration and nature of the reactive intermediates. If our preliminary conclusions are correct, a comparatively modest experimental program could lead to a rational model for predicting the reactivities of saturated organic compounds in "real life" environments and eliminate the need for expensive experimental evaluation of each separate compound.

V EXPERIMENTAL METHODS

The smog chamber used in this study has been described in a paper[14] accepted for publication in Environmental Science and Technology. The text of this paper is given in Appendix A. Experimental methods are described below.

For a typical experimental run, the chamber was swept with pure air at approximately 20 cfm for 9 to 15 hours while the chamber temperature was maintained at 40°C to 50°C with the lights on. The lights then were turned off, the cooling air turned on, and the chamber temperature lowered to 29°C. The pure air stream was diverted, and the chamber was sealed. The nitrogen dioxide and nitric oxide content of the chamber was measured, and sufficient nitrogen dioxide was metered into the chamber to raise the nitrogen oxides concentration to the desired level. The nitrogen dioxide was provided from a supply cylinder as a mixture with nitrogen (nitrogen dioxide content 3890 ppm). Similarly, propylene and butane were added as a mixture with nitrogen containing 1.48% butane and 0.38% propane. For the addition of solvents normally liquid at room temperature, the desired quantity of liquid was added to a U trap and vaporized into the chamber in a stream of air heated to near the boiling point of the liquid. The reactants were mixed by means of sonic pumps, initial concentration measurements were made, and the lights turned on. Measurements of concentrations of reactants and products were made at intervals throughout the day and plotted against time, zero time being the point at which the lights were turned on. Eye irritation usually was measured at two times, about 6 and 7 hours from time zero.

Nitrogen dioxide (NO_2) and nitric oxide (NO) were determined colorimetrically according to "Selected Methods for the Measurement of Air Pollutants" (U.S. Department of Health, Education, and Welfare, 1965). A suction pump was used to draw air from the chamber through glass tubing to a fritted glass bubbler containing the appropriate sampling solution. A timer and a flowmeter attached to the end of the sampling train were used to determine the volume of air being sampled. Sample requirements varied from 1 to 6 liters per analysis, depending on the concentration of the compound being analyzed.

Oxidant was measured with a Mast meter and ozone was determined by the gas phase titration method of Bufalini[15] also using the Mast meter. In experiments in which the Bufalini method was used to analyze mixtures of pure air and ozone in the 0.2 to 0.8 ppm range (no other oxidants present), we found throughout the range of ozone concentrations that the gas phase titration caused the Mast meter readings to fall to 0.02 ppm rather than 0.00 ppm, as expected in the analysis of ozone. The experimental ozone

values have been corrected by adding 0.02 ppm to each of them to account for this phenomenon. The total oxidant values have been corrected for the contribution of nitrogen dioxide; we find with our Mast analyzer that nitrogen dioxide gives a reading equal to 8% of its concentration.

PAN and certain organic reactants--diacetone alcohol, cellosolve acetate, and occasionally n-butyl acetate, diethyl cellosolve, Freon 113, and 1,1,2-trichloroethane--were measured by an infrared spectrophotometer, which had the optics of one of the long path (40-meter) cells located within the chamber volume. The absorptivity for infrared determination of peroxyacetyl nitrate was taken from the literature;[16] the absorptivities for the other compounds were determined by us. The limits of detectability for PAN, Freon 113, and 1,1,2-trichloroethane were about 0.05 ppm; the rest of the compounds were detectable at about 0.2 ppm.

Most of the organic reactants were measured by gas chromatography. An Aerograph hydrogen flame detector and column oven were used along with a Keithley Model 610A electrometer and a 10-inch Bristol recorder with a 1-mv span. The column for most runs was a $\frac{1}{16}$-inch-diameter tube 3 feet long filled with Proapak Q; for some runs with high-boiling test compounds where a background mix was not used, a similar column 14 inches long was employed. Column temperatures of 180°-190°C were used. Samples were injected into the chromatograph by using an 8-port valve fitted with a sample loop. For the first 44 runs, 60-ml gas samples were used and were concentrated by passage through a packed sample loop cooled in liquid oxygen. Subsequent runs were made using 0.7-ml gas samples without a freeze-out concentration step; this latter method gave more reproducible results.

Light intensity in the chamber has been discussed in detail by Doyle.[14] For the experiments reported herein, the chamber was illuminated by a combination of 50 sunlamps (FS 40), 28 blacklights (F40BL), 30 blue lamps (F40B), and 72 daylights (F72T 12D/VHO) that gave an integrated intensity between 300-400 nm of 11 x 10^{15} to 14 x 10^{15} quanta/sec cm^2 or 60% to 80% of noonday sunlight. Light intensity was monitored by a modified version of the o-nitrobenzaldehyde actinometer.[17]

Eye irritation was evaluated by a panel of nine individuals hired specifically for this task. Each individual was selected for greater-than-average sensitivity to eye irritation, consistency of responses, and freedom from medical problems (such as allergies) that might cause eye irritation. Each panelist was fitted with polyethylene welding goggle frames that were padded with silicone rubber to fit the contours of his face. The goggle frames were coupled to the chamber ports through a sliding gate valve arrangement. The eyeports were designed in such a way that no direct light reached the subjects' eyes. The eyeport valves were kept closed at all times except when the subjects were exposing their eyes. During the exposure, chamber

air was moved past the subjects' eyes at a controlled rate by means of a sonic pump in each eyeport. The eyeports were separated by partitions to prevent a subject from observing the response of subjects on either side of him.

The subjects were exposed to the chamber's contents in groups of four or five. Assignments of subjects to a particular group or to a particular eyeport location were randomized. In a typical run, the following sequence of operations was followed. The subjects were assigned eyeport locations and, when they were in position, a signal to start was given. At the signal, each subject placed his head in contact with the goggles and opened the eyeport valve. A maximum exposure time of 240 seconds was used; all subjects stayed in position for the entire period so that no subject would know how the others responded. During a test session, each panelist was subjected to two exposures about 10 minutes apart; values from both exposures were used to calculate a mean value, as described below. During the sequence of tests involving eye irritation measurements, the panelists were exposed to pure air (nonirritating) and 0.5 ppm chloropicrin (severely irritating) approximately once every two weeks to give them a frame of reference for their other judgements.

At the completion of a test session we had a body of data made up of the subjects' names, their eyeport assignments, and their response times (or a record of their failure to experience irritation in 240 seconds). The eyeport location had no influence on a subject's response. In general, each subject can be characterized on the basis of his deviation from the average panel response, and he will deviate consistently throughout the entire series of runs. Thus, we can anticipate that certain subjects will always respond first and certain other subjects will respond last or not at all. During the course of a program lasting several months, the makeup of the eye irritation panel necessarily varies from time to time, and the data must be treated in some way to minimize the bias created by the absence of a particularly sensitive (or insensitive) subject. Any data treatment procedure must also be able to handle response times about which we know only that they are greater than 240 seconds (the maximum exposure time).

Panel response times have been quantitated by various methods, some of which are:

1. Number of positive responses
2. Arithmatic mean, seconds
3. Median, seconds
4. Log probability distribution, equivalent seconds

5. Index calculated as $\frac{t_{max}-t}{t_{max}} \times 10$

6. Index calculated as $\log \frac{t_{max}}{t_{50}}$

The indices were devised to present data in such a way that the value of the index increased with increasing eye irritation; most of the other methods give an inverse relationship between the numerical value and the severity of irritation. Method 1, counting the number of positive responses, is crude, results in biased results if panel members are absent, and does not really use all of the data. Method 2, the arithmatic mean, usually means assigning an arbitrary value to all of the "no response" times and thus does not give a true mean value; it also gives biased results when the panel membership changes. Method 3 is satisfactory for handling "no response" times but still gives biased values if the panel membership varies. We prefer Method 4 because it handles "no response" times and minimizes variations due to changes in panel makeup. Our use of this procedure for calculating a mean eye irritation index is based on the assumption that, in the population represented by the panel, the response times to a given concentration of eye irritant will be log normally distributed. The panelists' response times were therefore plotted on log-probability paper, and the best-fitting straight line drawn through them. The ordinate value (t_{50}) of the intersection of this line with the 50 percentile abscissa was taken as the best estimate of the median response time for the population. The eye irritation index is defined as the log of the ratio of the maximum exposure time employed (240 seconds) to the log mean response time, t_{50}, that is, eye irritation index = log $240/t_{50}$. This index occasionally yields negative values, but we see no particular difficulties arising from this property.

For 16 pure air runs, the mean eye irritation index was 0.00 with a standard deviation of 0.10. For nine chloropicrin runs, the mean index was 0.88 with a standard deviation of 0.10. We attribute these deviations to the natural variability of human response caused by many factors over which the experimenter has no control. This variability requires that many replicate experiments be done to detect small differences in eye irritation index. For experimental programs such as the one described here, where only duplicate runs were made, only comparatively large differences in levels of eye irritants are detectable.

Aerosol measurements were made with a 90° light-scattering photometer of the O'Konski-Doyle type (a prototype of the Royco). The scattering of pure air was defined as a scattering unit of one (helium was used as a zero reference point), and all light-scattering values were normalized to the air value.

ACKNOWLEDGEMENTS

The experimental work was performed by Alan Hansen, Irwin Sauer, and Barbara Kurtin, with assistance from Gloria Keshtkar.

REFERENCES

1. Altshuller, A. P., Intern. J. Air Water Pollution, 10, 713 (1966)

2. Altshuller, A. P., and J. J. Bufalini, Photochem. Photobiol., 4, 97 (1965)

3. Bufalini, J. J., and A. P. Altshuller, Environ. Sci. Tech., 1, 133 (1967)

4. Dimitriades, B., B. H. Eccleston, and R. W. Hurn, "An Evaluation of the Fuel Factor Through Direct Measurement of Photochemical Reactivity of Emissions," presented at 62nd Annual Meeting of the Air Pollution Control Association, New York, June 22-26, 1969

5. Dimitriades, B., and M. L. Whisman, "Aldehyde/Olefin Interaction in NO_x-Sensitized Photooxidation of Aliphatic Olefins," presented at General Motors Symposium on Chemical Reactions in Urban Atmospheres, Warren, Michigan, October 6-7, 1969

6. Wilson, Katherine W., G. J. Doyle, D. A. Hansen, and R. D. Englert, "Measurement of Reactivities of Trichloroethylene and Other Solvents," paper submitted September 1969 for publication in Environ. Sci. Tech.

7. Altshuller, A. P., J. Air Pollution Control Assoc., 16, 257 (1966)

8. Benson, Sidney W., Thermochemical Kinetics, J. Wiley, New York, 1968, pp. 99-102 and especially pp. 100-101

9. Kaufman, Frederick, "Elementary Gas Reactions," Ann. Rev. Phys. Chem., 20, 45-90 (1969)

10. Herron, J. T., J. Chem. Phys., 45, 1854 (1966)

11. Baulsch, Drysdale, and Lloyd, High Temperature Reaction Rate Data. I, The University at Leeds, Phys. Chem. Dept., 1968

12. Greiner, N. R., J. Chem. Phys., 46, 2795 (1967)

13. Dixon-Lewis, G., W. E. Wilson, and A. A. Westenburg, J. Chem. Phys., 44, 2877 (1966)

14. Doyle, G. J., "Design and Performance of a Facility (Smog Chamber) for Studying Photochemical Reactions Under Conditions Simulating the

Tropospheric Atmosphere," accepted for publication in Environ. Sci. Tech. (1970)

15. Bufalini, J. J., Environ. Sci. Tech., 2, 703 (1968)

16. Stephens, E. R., Anal. Chem., 36, 928 (1964)

17. Gordon, R. J., "Photochemical Measurements," in Pilot Study of Ultraviolet Radiation in Los Angeles, ed. by J. S. Nader, Public Health Service Publication No. 999-AP-38, U.S. Dept. of Health, Education, and Welfare, Cincinnati, Ohio, 1967, pp. 37-47

ILLUSTRATIONS

Figure 1

RANKINGS BASED ON NORMALIZED MAXIMUM OXIDANT

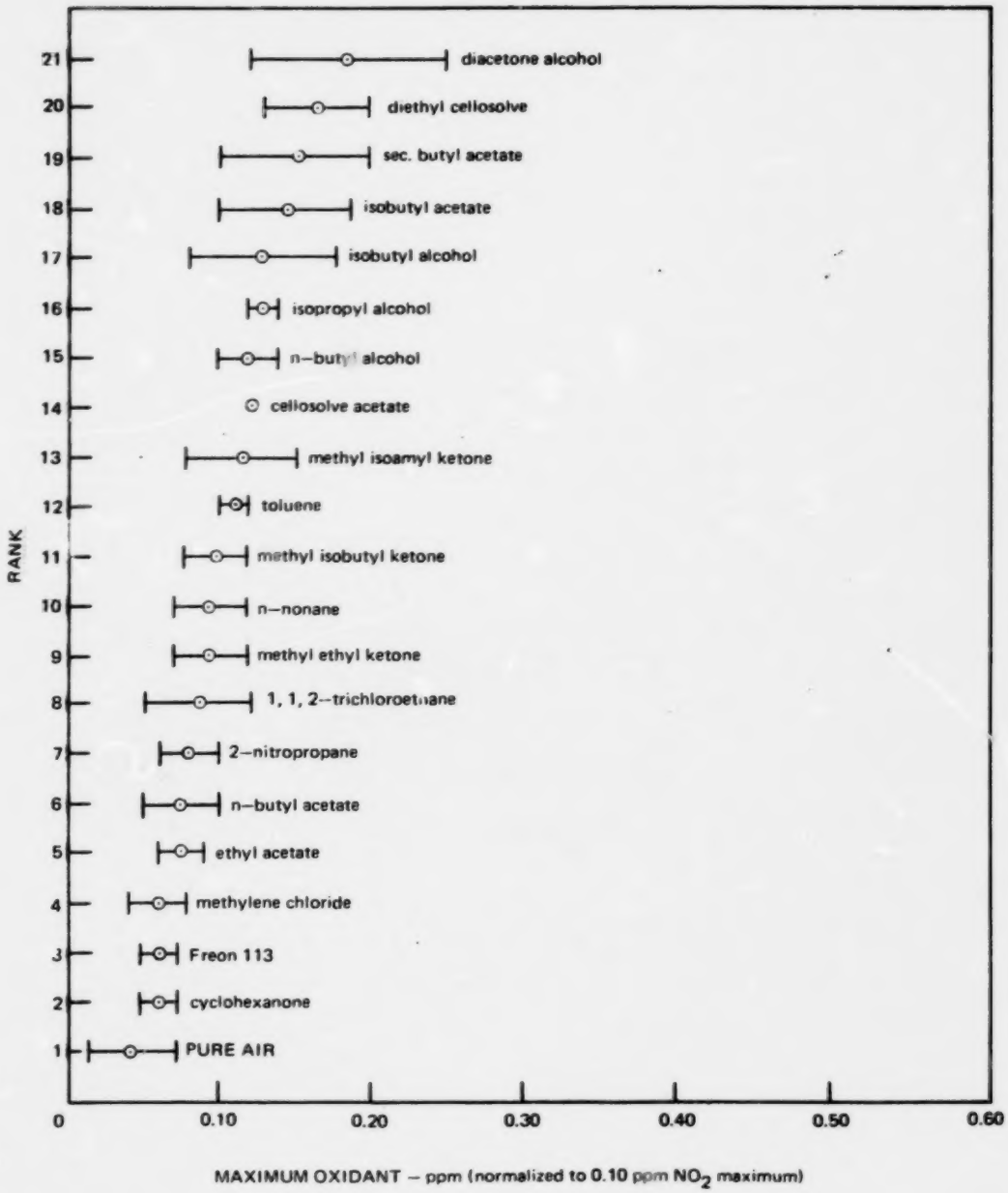


Figure 2

RANKINGS BASED ON SOLVENT REACTION RATE

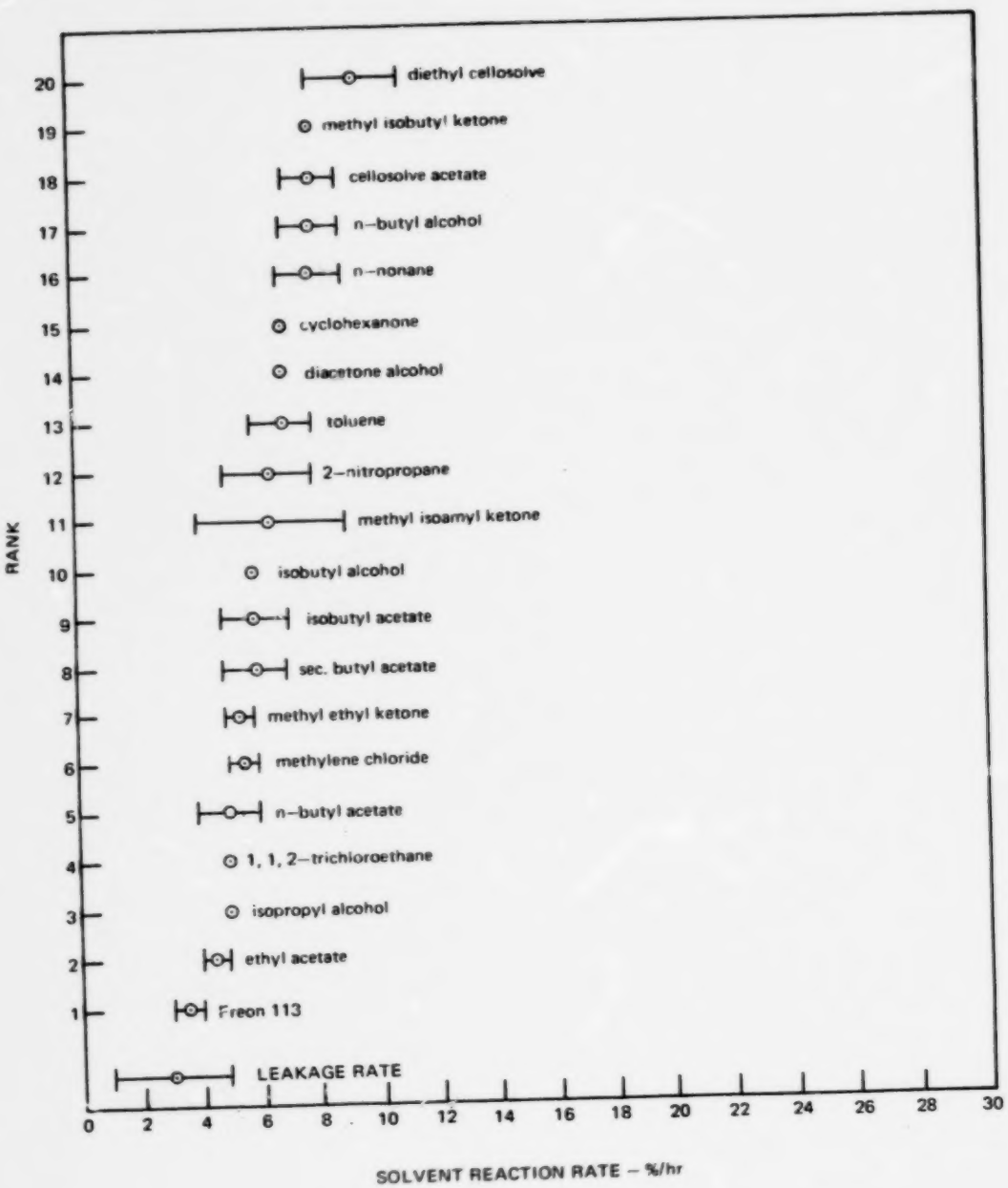


Figure 3

RANKINGS BASED ON OXIDANT DOSAGES IN RUNS
WITH BACKGROUND MIX PLUS 8 PPM TEST SOLVENT

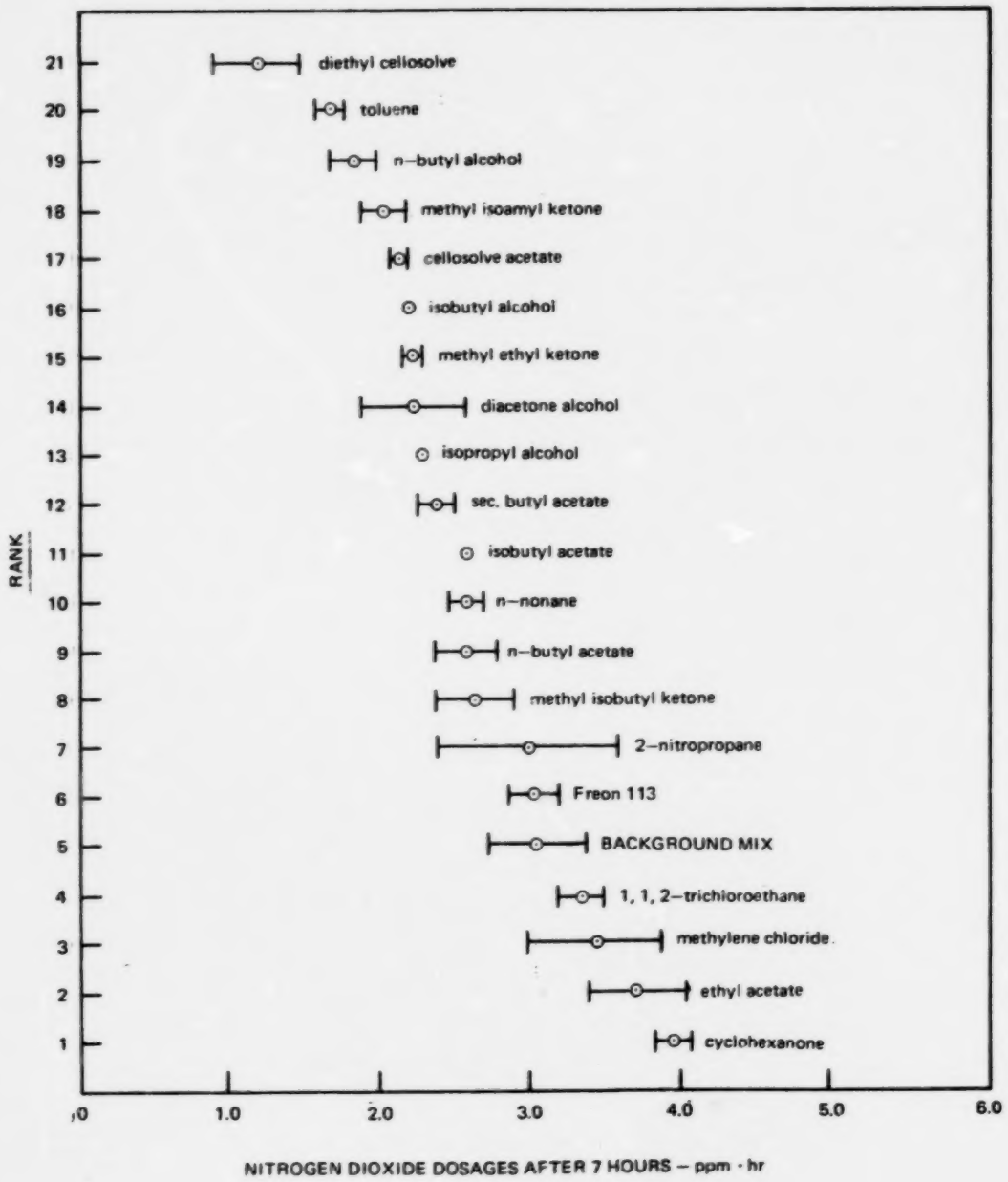


Figure 4

RANKINGS BASED ON NITROGEN DIOXIDE DOSAGES IN RUNS WITH BACKGROUND MIXES PLUS 4 PPM TEST SOLVENT

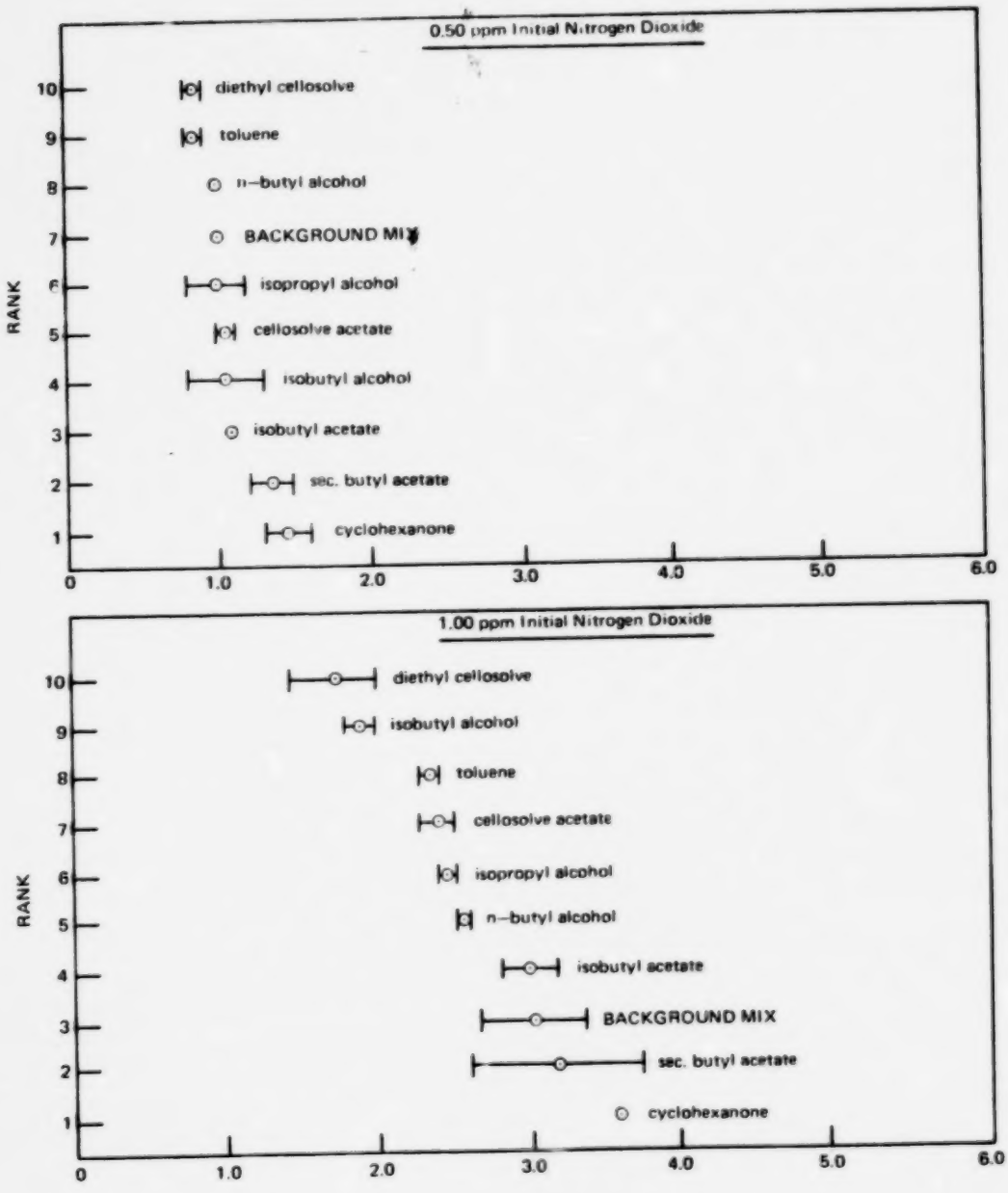


Figure 5

RANKINGS BASED ON NITROGEN DIOXIDE HALF-LIVES IN RUNS WITH BACKGROUND MIX PLUS 8 PPM TEST SOLVENT

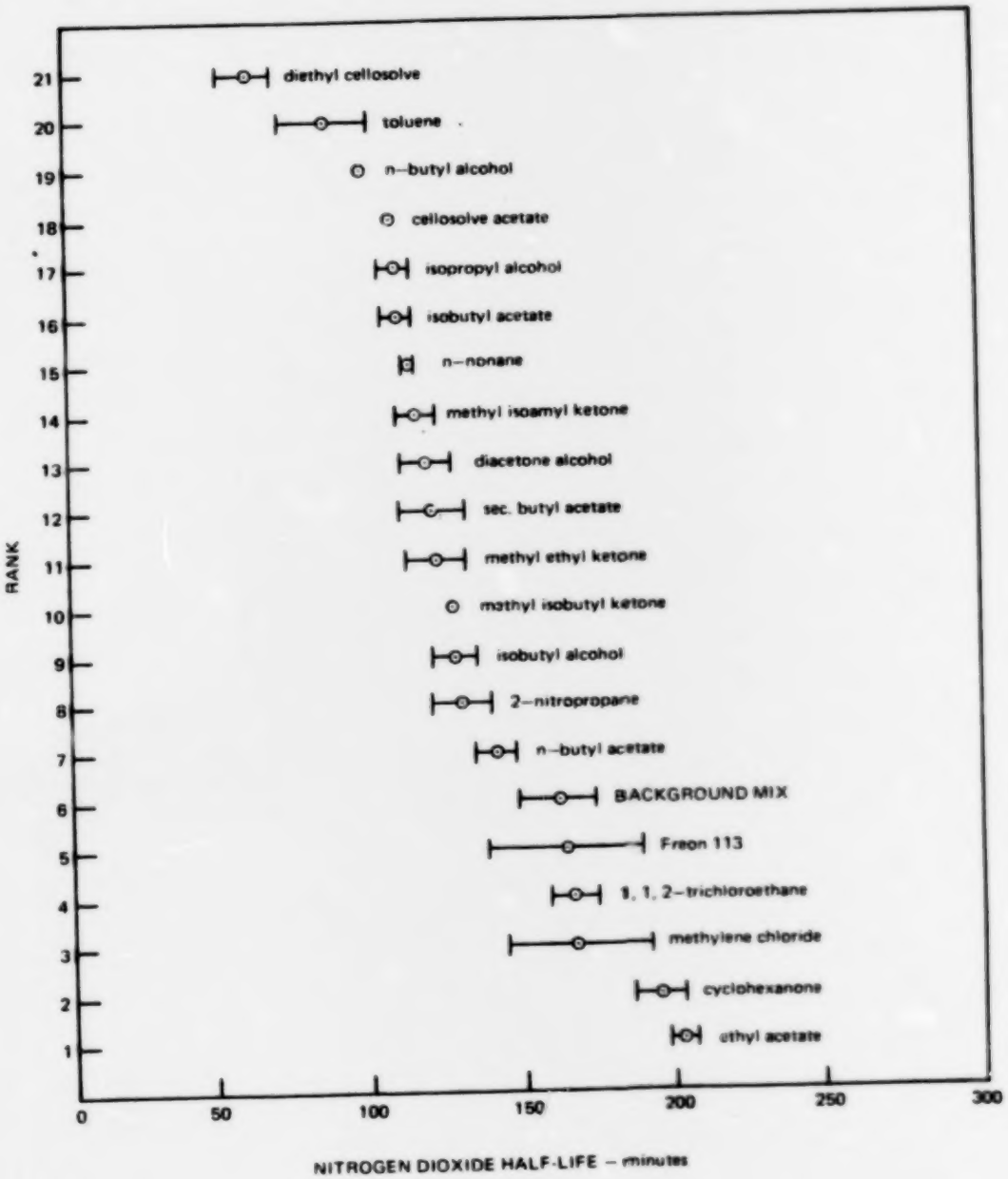


Figure 6

RANKINGS BASED ON NITROGEN DIOXIDE HALF-LIVES IN RUNS WITH BACKGROUND MIXES PLUS 4 PPM TEST SOLVENT

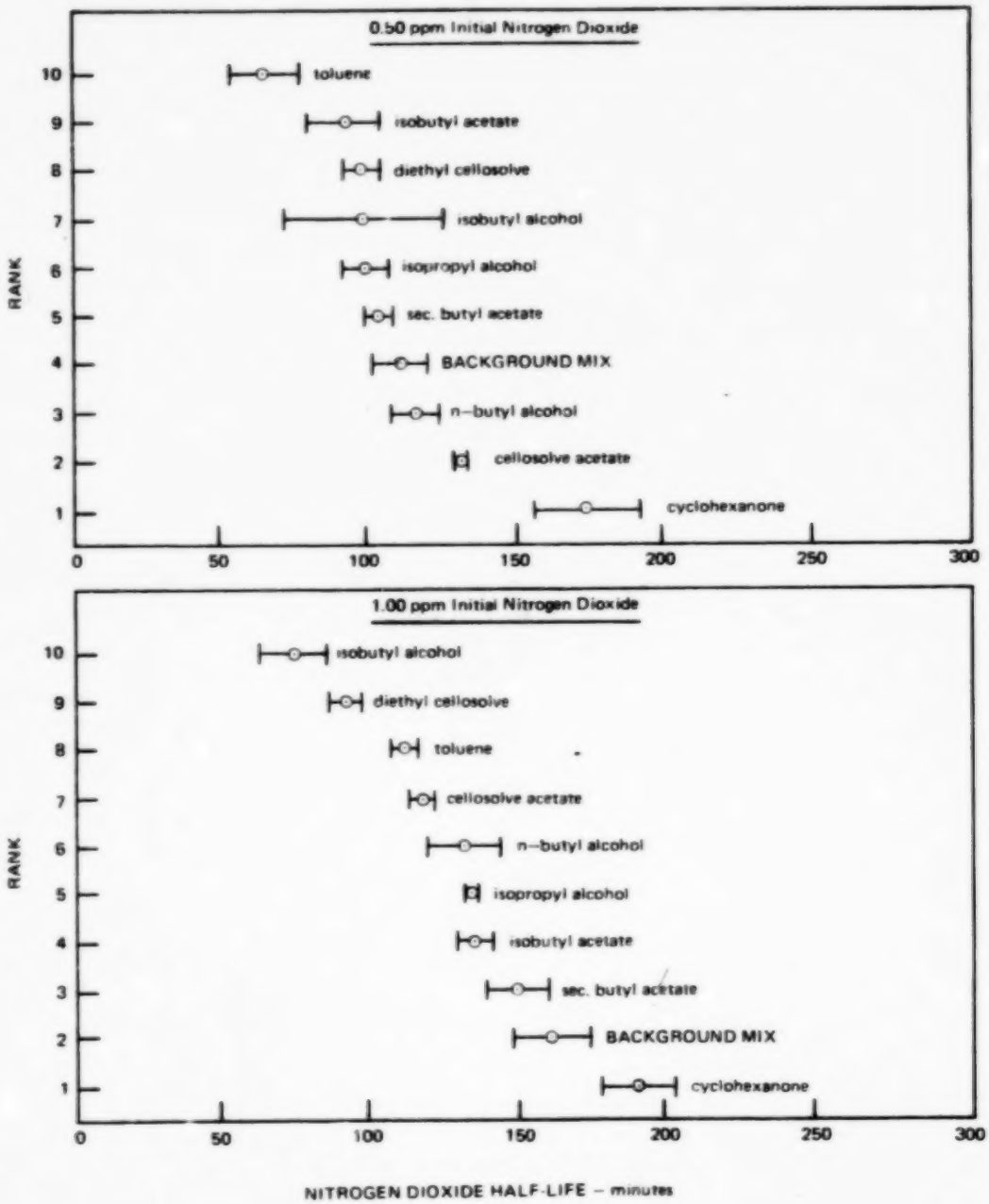


Figure 7

RANKINGS BASED ON OXIDANT MAXIMA IN RUNS WITH BACKGROUND MIX PLUS 8 PPM TEST SOLVENT

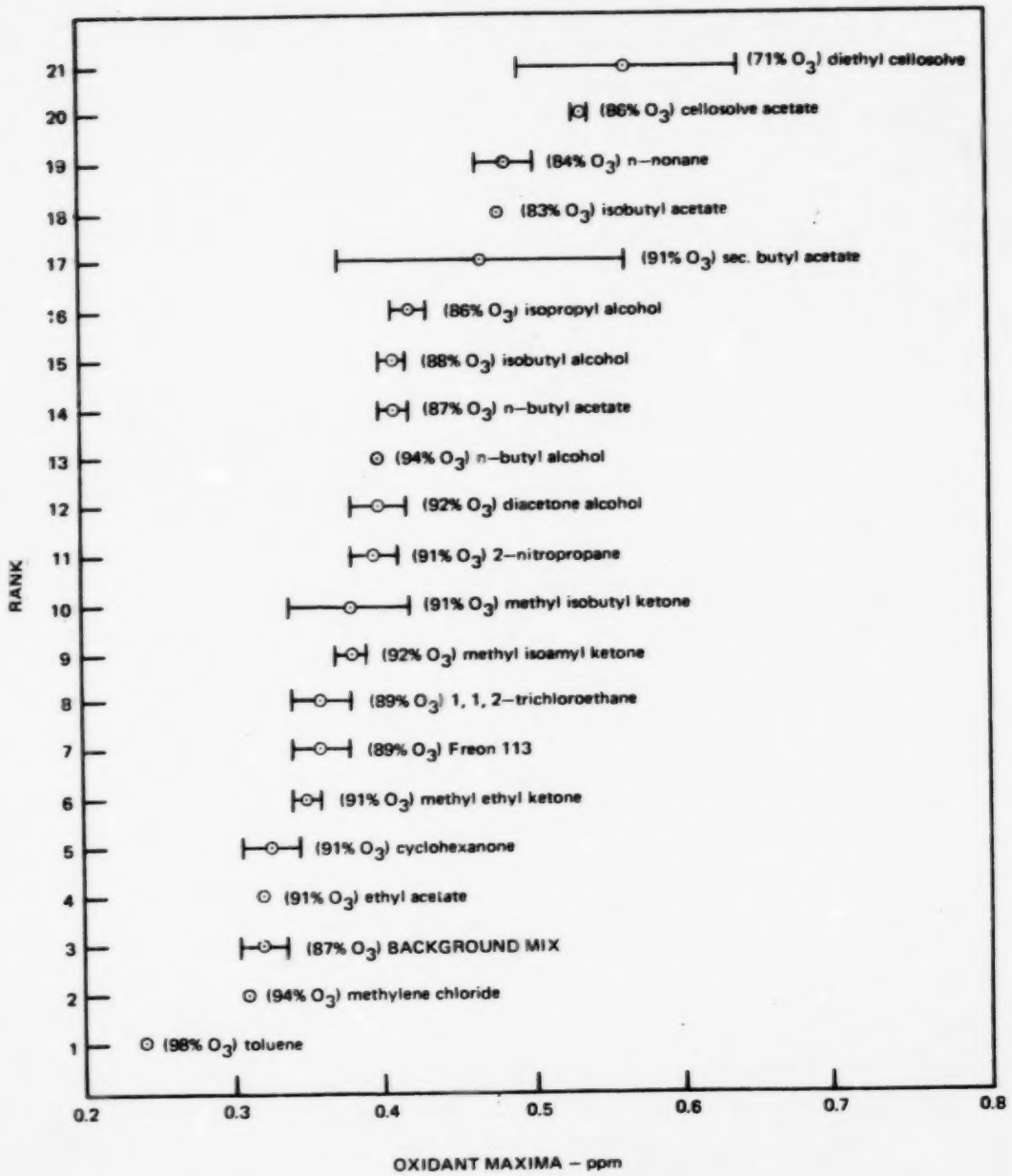


Figure 8

RANKINGS BASED ON OXIDANT MAXIMA IN RUNS WITH BACKGROUND MIXES PLUS 4 PPM TEST SOLVENT

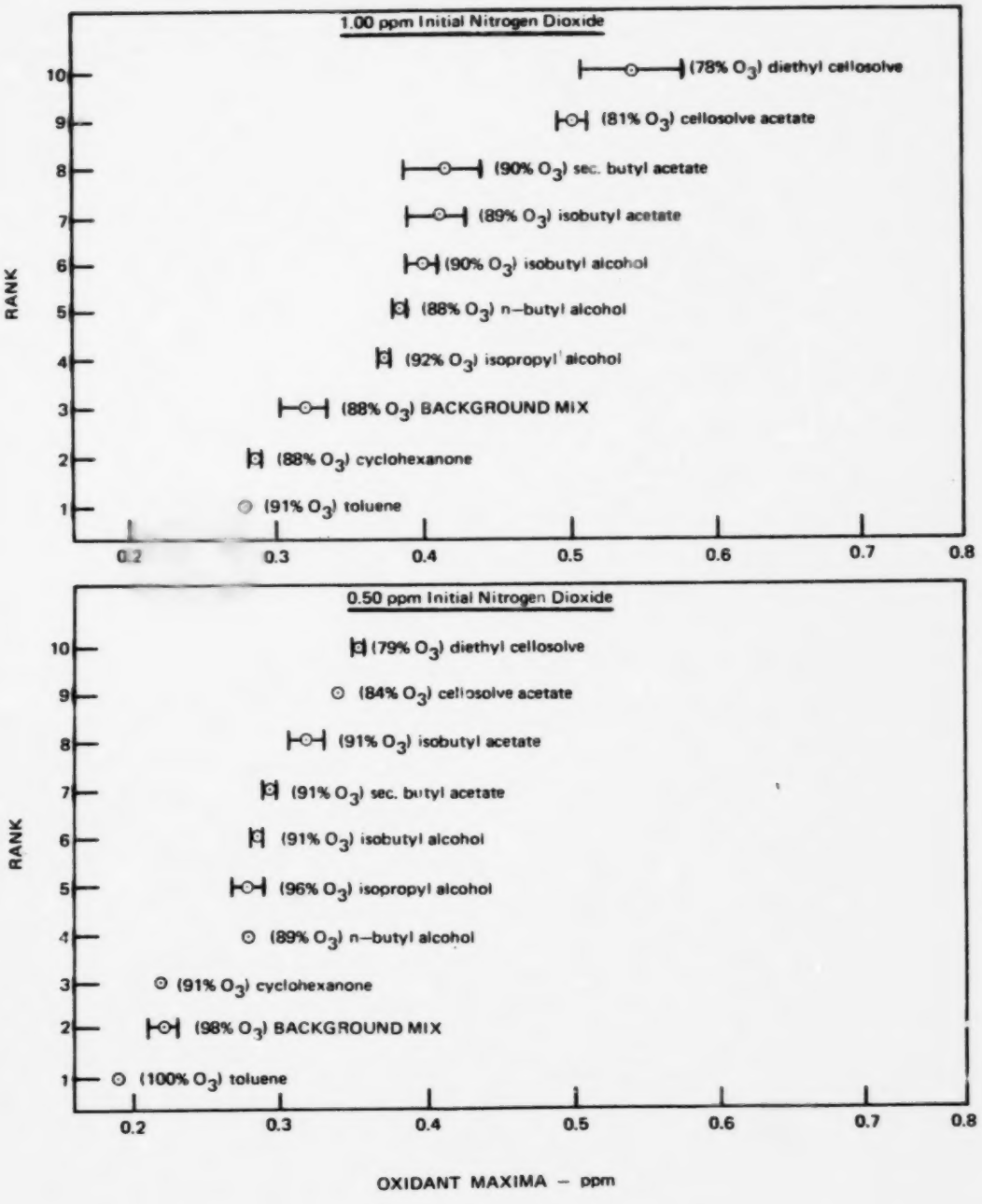


Figure 9

RANKINGS BASED ON OXIDANT DOSAGES IN RUNS WITH BACKGROUND MIX PLUS 8 PPM TEST SOLVENT

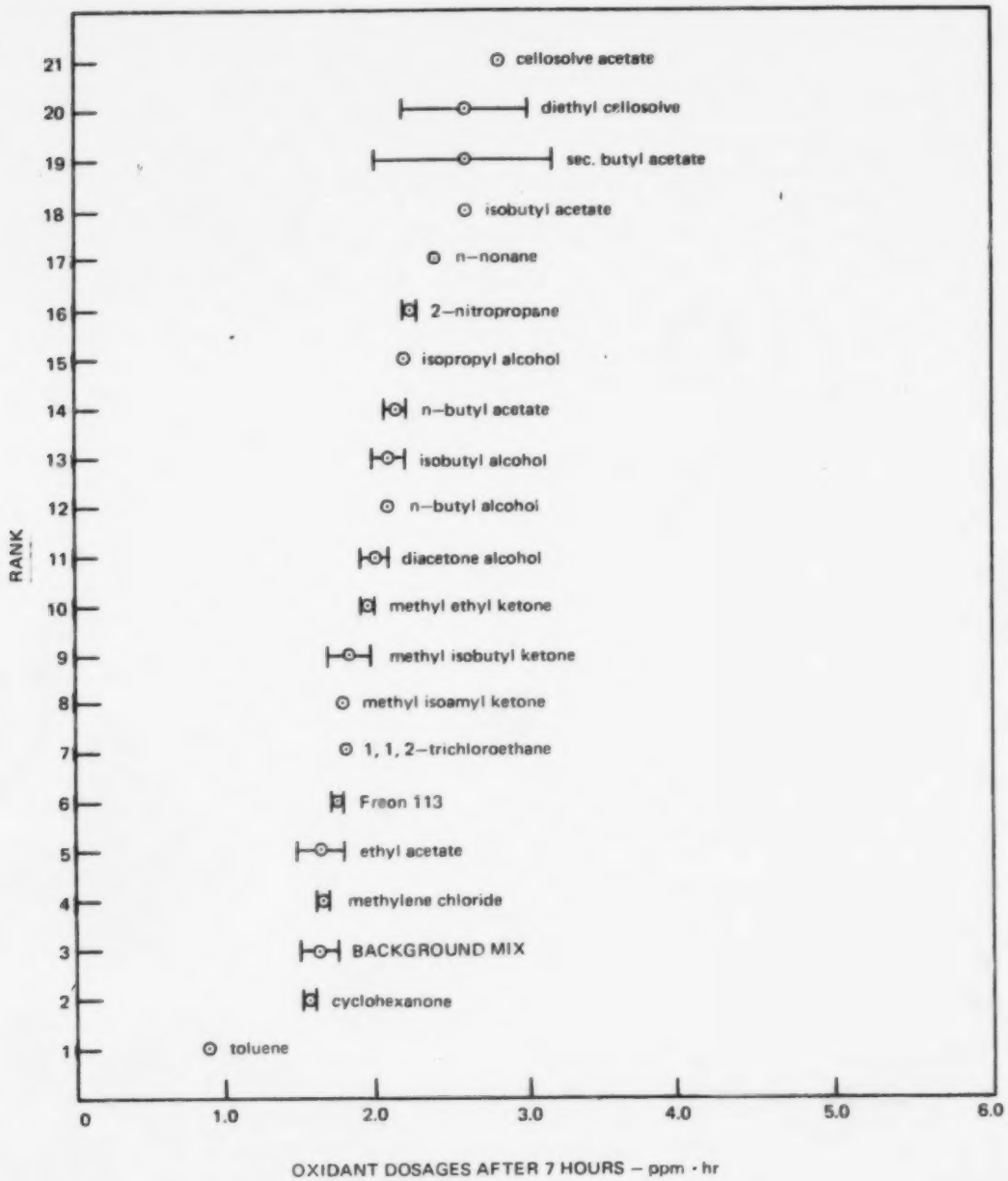


Figure 10

RANKINGS BASED ON OXIDANT DOSAGES IN RUNS WITH BACKGROUND MIXES PLUS 4 PPM TEST SOLVENT

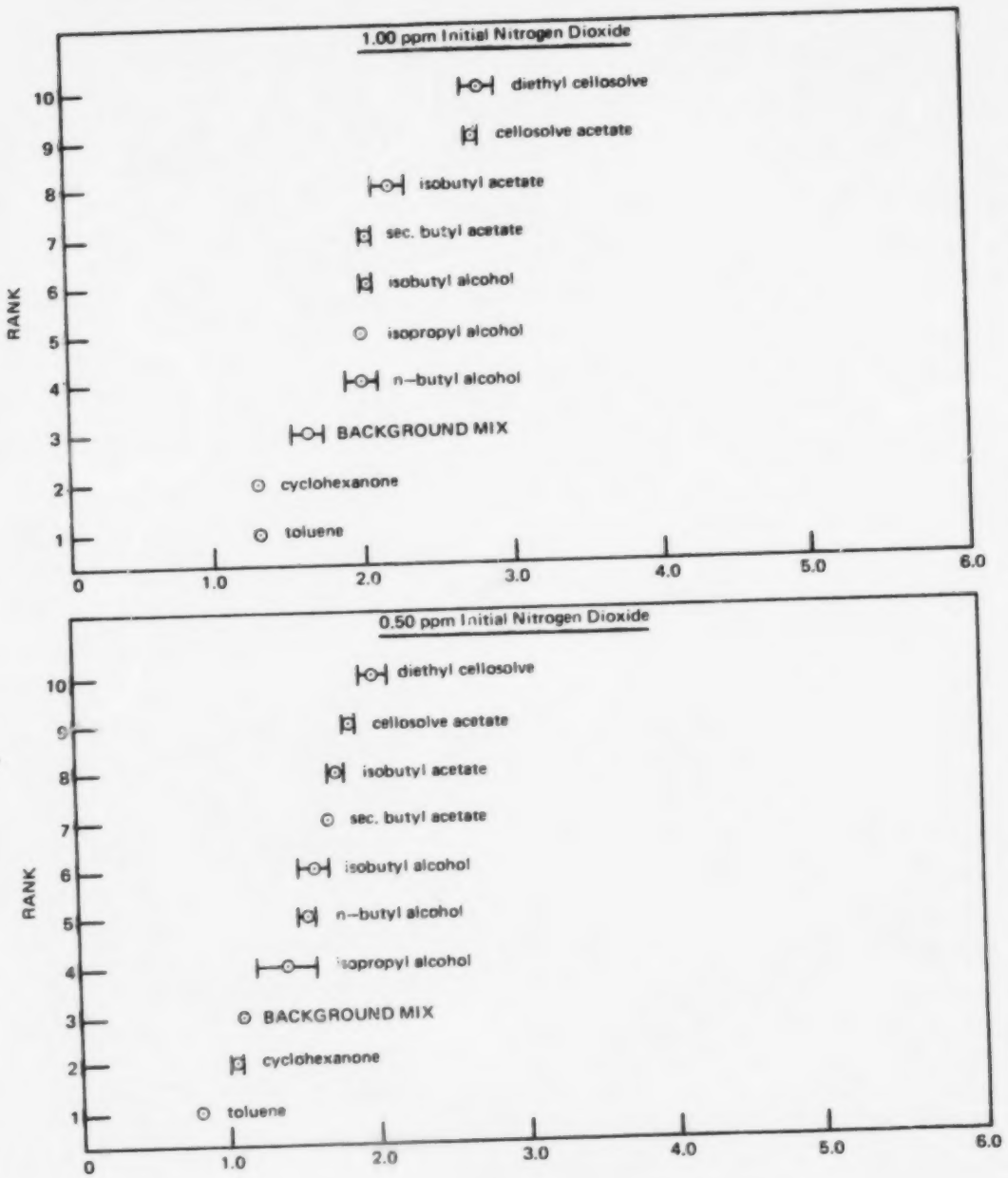
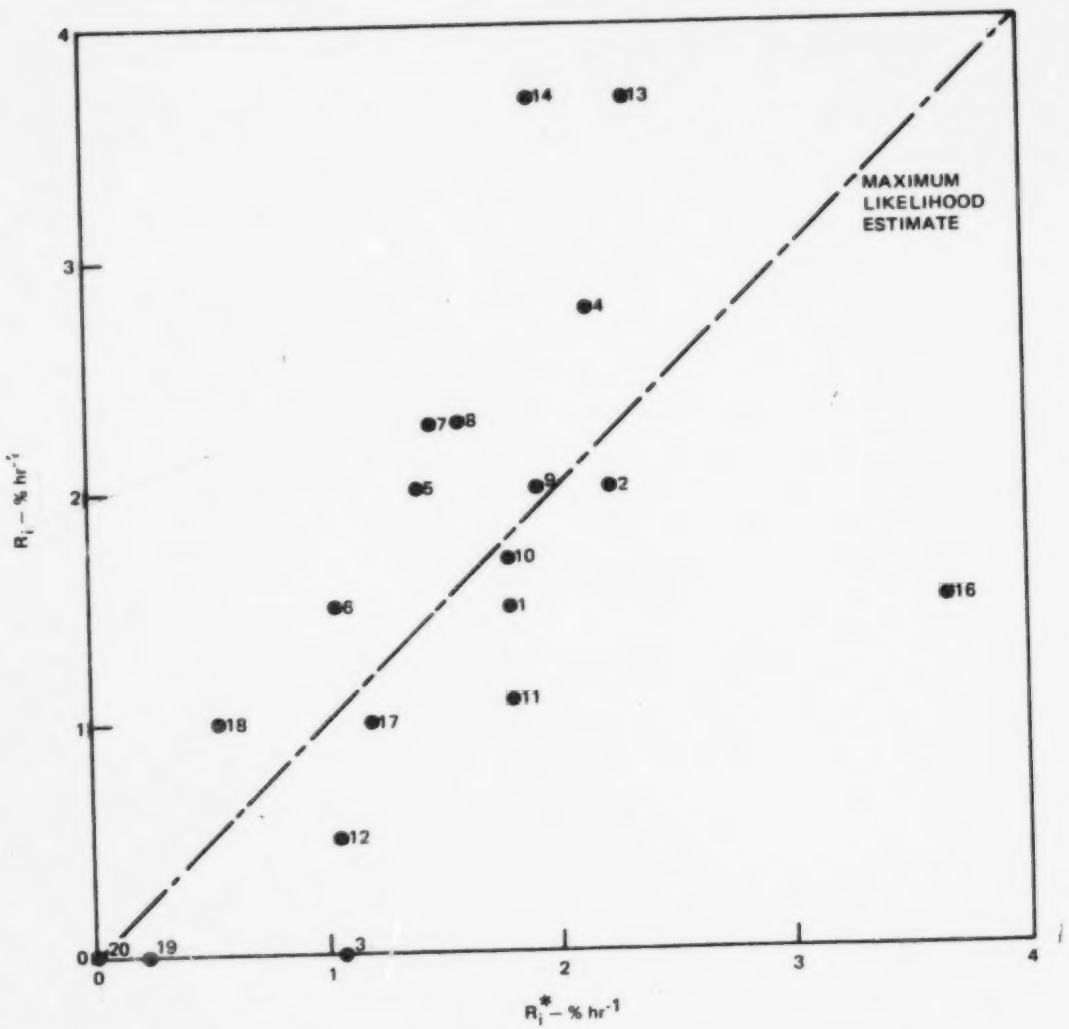


Figure 11

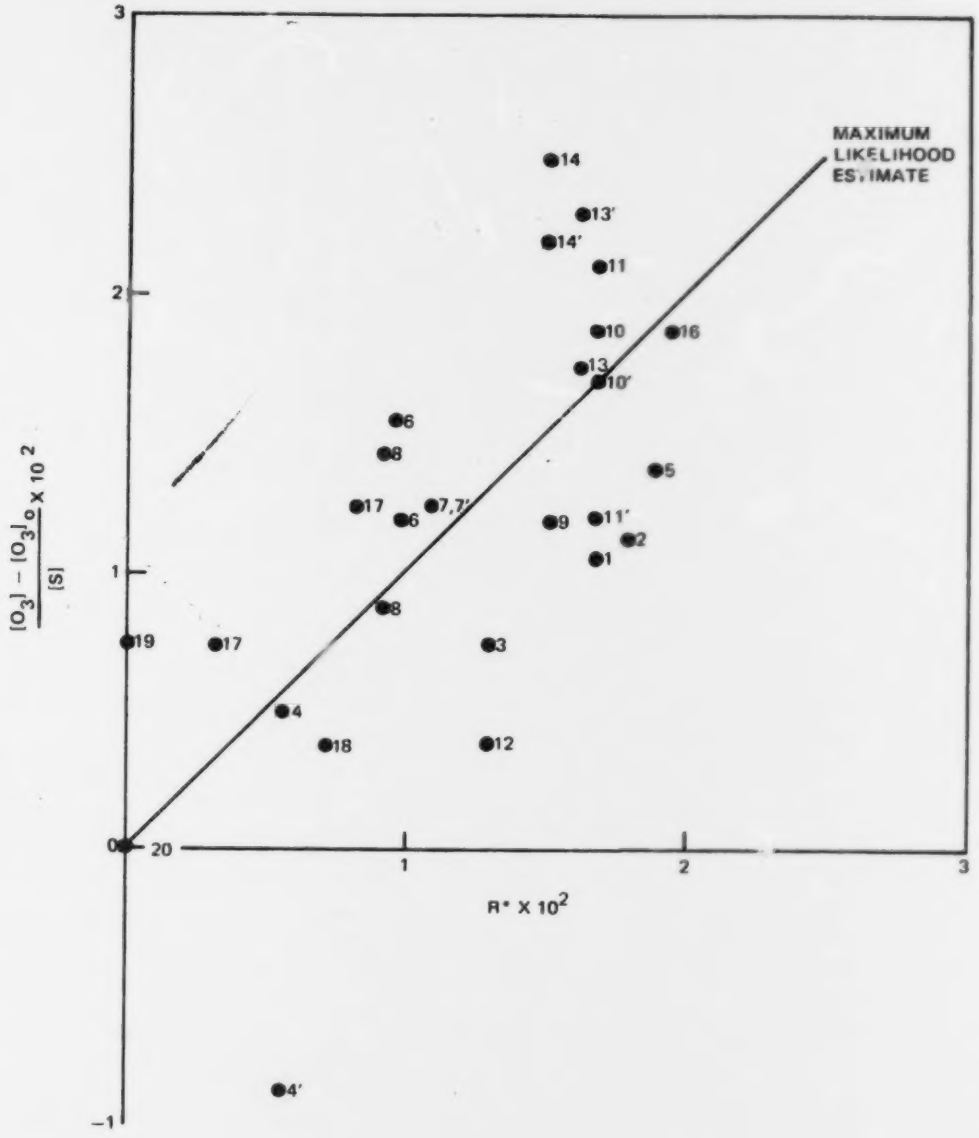
PREDICTED VS CALCULATED RATES OF
DISAPPEARANCE OF TEST SOLVENTS



NOTE: See Table 8 for identification of numbers.

Figure 12

PREDICTED VS CALCULATED INCREASE IN MAXIMUM OZONE



NOTES: See Table 8 for identification of numbers.
Prime after numbers indicates initial solvent concentration was 4 rather than 8 ppm.

TABLES

Table 1

IRRADIATION EXPERIMENTS WITH TEST SOLVENTS AND NITROGEN OXIDES

Initial Hydrocarbon	Initial NO_x NO (ppm)	Initial NO_x NO_2 (ppm)	Solvent Reaction Rate (%/hr)	NO_2 Dosage After 4 Hrs (ppm·hr)	NO_2 Dosage After 7 Hrs (ppm·hr)	Ozone Maximum (ppm)	Oxidant Maximum (ppm)	Oxidant Normalized Maximum[a] (ppm)	Oxidant Dosage After 4 Hrs (ppm·hr)	Oxidant Dosage After 7 Hrs (ppm·hr)	Eye Irritation Indices	Statistical Comparison: Solvent vs Irradiated Pure Air t	Statistical Comparison: Solvent vs Irradiated Pure Air df	Maximum Aerosol (sq/cu)	Man Number
None (pure air)	0.05	0.09	--	0.4	0.7	0.06	0.06	0.07	0.1	0.2	-0.05, -0.35			1.2	226
	0.06	0.10	--	0.6	1.1	0.01	0.01	0.01	0.0	0.0	0.00, 0.00			None	292
	0.03	0.12	--	0.5	0.6	0.02	0.02	0.02	0.0	0.1	0.00, 0.09			None	330
Methyl isobutyl ketone	0.03	0.06	(b)	0.2	0.3	0.10	0.10	0.12	0.2	0.3	-0.00, 0.00	0.16	4	1.3	209
	0.07	0.17	8	0.6	0.8	0.15	0.15	0.08	0.3	0.7	(0.23, 0.34)			1.1	265
Methyl isoamyl ketone	0.15	0.03	4	0.5	0.7	0.11	0.11	0.08	0.2	0.4	0.20, 0.13	0.71	6	1.7	203
	0.05	0.05	9	0.2	0.3	0.08	0.08	0.15	0.2	0.4	0.00, 0.00			1.2	242
Methyl ethyl ketone	0.03	0.11	5	0.5	0.7	0.13	0.14	0.12	0.2	0.4	0.00, 0.25	0.44	6	1.6	229
	0.05	0.13	6	0.6	0.9	0.10	0.11	0.07	0.1	0.3	-0.18, 0.13			1.1	291
Cyclohexanone	0.06	0.09	7	0.4	0.7	0.09	0.09	0.07	0.1	0.4	-0.37, -0.13	0.84	6	1.4	239
	0.09	0.11	7	0.5	0.7	0.07	0.08	0.06	0.1	0.3	(0.16, 0.26)			1.1	294
Diacetone alcohol	0.06	0.14	7	0.7	0.8	0.20	0.22	0.12	0.4	0.9	0.14, 0.06	0.83	5	1.4	226
	0.06	0.07	(b)	0.4	0.5	0.24	0.27	0.25	0.6	1.4	0.00			1.2	241
Isopropyl alcohol	0.12	0.02	5	0.3	0.5	0.11	0.12	0.14	0.2	0.5	0.03, -0.05	0.20	6	2.3	200
	0.07	0.05	5	0.4	0.6	0.12	0.12	0.12	0.3	0.6	-0.07, 0.04			1.3	231
Isobutyl alcohol	0.04	0.06	6	0.2	0.3	0.11	0.11	0.16	0.3	0.6	0.00, 0.00	1.17	6	1.2	215
	0.07	0.05	8	0.7	1.1	0.16	0.17	0.08	0.6	1.9	0.30, 0.24			1.5	242
n-Butyl alcohol	0.03	0.04	8	0.4	0.6	0.13	0.14	0.14	0.3	0.7	0.17, 0.17	1.09	5	1.7	230
	0.09	0.11	7	0.5	0.8	0.13	0.14	0.10	0.4	0.7	0.00			1.2	286
n-Butyl acetate	0.03	0.18	4	0.7	1.1	0.10	0.10	0.05	0.2	0.4	0.00	0.20	4	1.2	245
	0.13	0.07	6	0.4	0.6	0.11	0.12	0.10	0.4	0.7	0.06			1.2;	276
Isobutyl acetate	0.05	0.07	7	0.3	0.4	0.12	0.13	0.19	0.2	0.5	0.14	0.23	5	1.1	251
	0.19	0.10	5	0.6	0.9	0.17	0.18	0.10	0.5	1.0	-0.06, 0.00			1.2	274
Sec. Butyl acetate	0.03	0.07	5	0.2	0.4	0.14	0.14	0.20	0.4	0.8	-0.07, ≤0	1.36	6	1.4	238
	0.06	0.11	7	0.5	0.7	0.12	0.14	0.10	0.3	0.7	(0.43, 0.54)			1.1	263
Ethyl acetate	0.12	0.09	4	0.4	0.6	≤0.08	0.08	0.09	0.2	0.4	0.19, -0.10	0.47	5	1.9	204
	0.06	0.18	5	0.7	1.0	0.10	0.10	0.06	0.2	0.5	-0.12			1.4	284
Diethyl cellosolve	0.03	0.06	6	0.3	0.4	0.14	0.16	0.20	0.4	0.9	0.05, 0.02	1.47	6	1.6	206
	0.09	0.19	11	0.7	0.9	0.24	0.28	0.13	0.6	1.6	(0.40, 0.37)			1.4	260
Cellosolve acetate	0.06	0.10	7	0.6	0.8	0.16	0.18	0.12	0.5	0.9	0.06, 0.11	1.47	6	1.2	240
	0.01	0.15	9	0.6	0.8	0.18	0.20	0.12	0.6	1.0	0.32, 0.30			1.4	268
Toluene	0.04	0.08	8	0.2	0.2	0.06	0.06	0.10	0.2	0.4	0.03, -0.23	0.28	6	1.9	237
	0.10	0.06	6	0.3	0.3	0.10	0.10	0.12	0.4	0.6	0.01, 0.06			1.4	275
n-Nonane	0.02	0.12	9	0.4	0.6	0.12	0.14	0.12	0.3	0.7	0.26, 0.19	0.52	6	1.7	206
	0.11	0.16	7	0.7	1.1	0.12	0.13	0.07	0.2	0.5	-0.06, -0.06			1.2	241
2-Nitropropane	0.04	0.08	8	0.4	0.7	0.11	0.11	0.10	0.1	0.4	-0.40, -0.18	(c)	5	1.4	236
	0.08	0.06	5	0.6	1.2	0.09	0.10	0.08	0.1	0.3	-0.09			1.1	271
1,1,2-Trichloroethane	0.06	0.05	5	0.3	0.5	0.10	0.10	0.12	0.2	0.4	0.00, 0.00	0.10	6	1.9	207
	0.05	0.11	8	0.5	0.9	0.07	0.07	0.08	0.1	0.3	-0.10, 0.04			1.5	224
Methylene chloride	0.03	0.06	6	0.4	0.7	0.10	0.10	0.08	0.1	0.3	0.08, 0.08	0.81	5	2.6	223
	0.10	0.15	5	0.5	1.0	0.08	0.08	0.04	0.1	0.2	0.16			1.3	255
Freon 113	0.03	0.08	3	0.4	0.6	0.08	0.08	0.07	0.1	0.2	-0.40, -0.11	(c)	6	1.5	220
	0.09	0.10	4	0.4	0.7	0.06	0.06	0.05	0.1	0.2	0.00, -0.06			1.4	225

Note: Values in parentheses may be in error because of experimental irregularities.

a. See text for explanation.

b. Experimental difficulties prevented measurement.

c. Less irritating than pure air--too many negative indices to give an accurate value for t.

Test Solvent	Initial Concentration (ppm)	Background Mix No.	Initial NO_x NO (ppm)	Initial NO_x NO_2 (ppm)	NO_2 Half-Life (min)	NO_2 Dosage After 4 Hrs (ppm·hr)	NO_2 Dosage After 7 Hrs (ppm·hr)	Ozone Maximum (ppm)
None	0.00	1	0.19	0.89	168	2.6	3.0	0.26
	0.00	1	0.03	1.10	174	3.0	3.5	0.30
	0.00	1	0.05	1.12	141	2.8	3.3	0.29
	0.00	1	0.08	0.90	159	2.6	3.0	0.29
	0.00	1	0.10	0.86	165	2.1	2.5	0.29
	0.00	2	0.08	0.41	120	0.9	1.0	0.19
	0.00	2	0.07	0.47	102	0.9	1.0	0.20
Methyl isobutyl ketone	8.0	1	0.08	1.12	128	2.6	2.9	0.38
	8.0	1	0.06	0.91	126	2.1	2.4	0.31
Methyl isoamyl ketone	8.0	1	0.04	0.85	123	1.8	1.9	0.36
	8.0	1	0.02	1.05	111	2.0	2.2	0.34
Methyl ethyl ketone	8.0	1	0.05	0.97	112	2.0	2.2	0.30
	8.0	1	0.06	0.90	132	2.1	2.3	0.34
Cyclohexanone	8.0	1	0.04	1.10	204	3.2	3.9	0.28
	8.0	1	0.05	1.16	186	3.2	4.1	0.32
	4.0	1	0.12	0.80	204	2.8	3.6	0.26
	4.0	1	0.05	1.05	177	2.8	3.6	0.24
	4.0	2	0.14	0.38	156	1.1	1.3	0.19
	4.0	2	0.05	0.45	192	1.3	1.6	0.21
Diacetone alcohol	8.0	1	0.04	0.90	111	1.8	1.9	0.38
	8.0	1	0.06	1.08	129	2.5	2.6	0.36
Isopropyl alcohol	8.0	1	0.03	1.10	105	2.1	2.3	0.38
	8.0	1	0.04	1.01	115	2.1	2.3	0.39
	4.0	1	0.08	0.94	135	2.1	2.4	0.34
	4.0	1	0.07	0.96	132	2.3	2.5	0.35
	4.0	2	0.07	0.51	108	1.1	1.2	0.28
	4.0	2	0.12	0.37	93	0.7	0.8	0.26
Isobutyl alcohol	8.0	1	0.12	0.90	135	2.0	2.2	0.35
	8.0	1	0.03	1.05	120	2.1	2.2	0.37
	4.0	1	0.17	1.27	63	1.8	2.0	0.35
	4.0	1	0.05	0.93	87	1.6	1.8	0.37
	4.0	2	0.14	0.52	126	1.2	1.3	0.28
	4.0	2	0.18	0.40	72	0.6	0.8	0.24
n-Butyl alcohol	8.0	1	0.08	0.89	99	1.6	1.7	0.36
	8.0	1	0.25	0.99	99	1.8	2.0	0.39
	4.0	1	0.08	0.92	144	2.3	2.5	0.33
	4.0	1	0.06	1.07	120	2.4	2.6	0.35
	4.0	2	0.07	0.44	108	0.9	1.0	0.24
	4.0	2	0.10	0.38	123	0.9	1.0	0.26

Notes: Background Mix No. 1 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and NO_2 (1.0 pp
Background Mix No. 2 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and NO_2 (0.5 pp
Values in parentheses may be in error because of experimental irregularities.

a/ Experimental difficulties prevented measurement.

IRRADIATION EXPERIMEN
AND KETONE

ge ter 7 Hrs (ppm·hr)	Ozone Maximum (ppm)	Oxidant Dosage Maximum (ppm)	Oxidant Dosage After 4 Hrs (ppm·hr)	Oxidant Dosage After 7 Hrs (ppm·hr)	Hydrocarbon Disappearance Rate Propylene (%/hr)	Butane (%/hr)	Toluene (%/hr)	Test Solvent (%/hr)	PAN Dosage After 7 Hrs (ppm·hr)	Indices
3.0	0.26	0.29	0.6	1.5	35	7	9	None	0.8	0.20, 0.1
3.5	0.30	0.33	0.7	1.6	30	5	5	None	0.4	0.24, 0.0
3.3	0.29	0.33	0.7	1.6	30	5	6	None	0.3	0.19, 0.2
3.0	0.29	0.31	0.8	1.7	32	7	7	None	0.3	0.40, 0.5
2.5	0.29	0.32	0.8	1.7	35	6	8	None	0.2	-0.07, 0.0
1.0	0.19	0.21	0.7	1.1	40	5	7	None	0.1	0.00, 0.2
1.0	0.20	0.23	0.7	1.1	35	6	7	None	0.2	0.15, 0.1
2.9	0.38	0.42	1.0	2.0	27	5	6	7	0.4	0.08, 0.3
2.4	0.31	0.34	0.8	1.7	36	4	(a)	6	(a)	0.40, 0.5
1.9	0.36	0.39	1.1	1.8	40	5	5	8	Trace	0.10, 0.2
2.2	0.34	0.37	1.1	1.8	36	3	5	6	0.3	0.25, 0.4
2.2	0.30	0.34	0.9	1.9	35	5	8	5	(a)	0.11, 0.0
2.3	0.34	0.36	1.0	2.0	47	5	8	5	0.2	(0.19, 0.2
3.9	0.28	0.31	0.5	1.5	20	5	7	6	0.4	-0.08, 0.1
4.1	0.32	0.35	0.5	1.6	32	5	8	8	0.2	(0.41, 0.1
3.6	0.26	0.29	0.5	1.3	28	5	6	7	0.1	0.25, 0.2
3.6	0.24	0.28	0.5	1.3	25	6	7	8	Trace	0.18, 0.2
1.3	0.19	0.22	0.4	1.0	28	5	6	7	0.1	0.32, 0.3
1.6	0.21	0.22	0.5	1.1	26	5	6	8	Trace	0.23, 0.4
1.9	0.38	0.42	1.1	2.1	24	4	5	6	0.5	-0.05, -0.1
2.6	0.36	0.38	1.0	1.9	32	5	6	8	0.4	0.40, 0.4
2.3	0.38	0.41	1.2	2.2	38	5	7	7	0.4	0.07, 0.1
2.3	0.39	0.43	1.3	2.2	47	6	7	6	0.1	0.23, 0.3
2.4	0.34	0.37	1.1	2.0	40	6	7	7	0.1	0.30, 0.4
2.5	0.35	0.38	1.1	2.0	40	6	7	6	0.1	0.17, 0.2
1.2	0.28	0.29	1.0	1.6	36	6	6	6	0.1	-0.26
0.8	0.26	0.27	0.7	1.2	40	6	6	7	Trace	0.00, 0.1
2.2	0.35	0.40	1.1	2.0	30	5	8	7	0.3	0.43, 0.5
2.2	0.37	0.42	1.2	2.2	43	6	6	8	0.3	-0.08, 0.0
2.0	0.35	0.39	1.2	2.1	40	6	7	7	0.1	0.14
1.8	0.37	0.41	1.2	2.0	40	5	6	7	0.1	-0.02, 0.0
1.3	0.28	0.29	1.0	1.7	40	6	7	8	0.1	0.00, 0.0
0.8	0.24	0.28	0.9	1.5	37	5	6	7	0.1	0.15, 0.0
1.7	0.36	0.40	1.3	2.1	(25)	6	6	9	0.3	-0.02, -0.0
2.0	0.39	0.40	1.2	2.1	35	7	7	6	0.2	0.36, 0.0
2.5	0.33	0.38	1.0	1.9	35	6	7	8	0.1	0.20, 0.0
2.6	0.35	0.39	1.2	2.1	38	6	6	7	Trace	0.17, 0.0
1.0	0.24	0.28	0.9	1.6	38	6	9	8	0.1	0.06, 0.0
1.0	0.26	0.28	0.9	1.5	40	6	6	6	0.1	-0.04, 0.0

ppm), and NO_2 (1.0 ppm).
ppm), and NO_2 (0.5 ppm).
s.

B

Table 2

IRRADIATION EXPERIMENTS WITH STANDARD BACKGROUND MIXES AND KETONE AND ALCOHOL SOLVENTS

...on Disappearance Rate			PAN Dosage After 7 Hrs (ppm·hr)	Eye Irritation			Maximum Aerosol (air=1)	Run Number
...ane (%/hr)	Toluene (%/hr)	Test Solvent (%/hr)		Indices	Statistical Comparison: Solvent vs Background Mix t	df		
							2.1	1
7	9	None	0.8	0.20, 0.16			1.6	214
5	5	None	0.4	0.24, 0.08			1.8	222
5	6	None	0.3	0.19, 0.25			1.4	267
7	7	None	0.3	0.40, 0.54			1.2	289
6	8	None	0.2	-0.07, 0.08			1.1	317
5	7	None	0.1	0.00, 0.20			1.1	318
6	7	None	0.2	0.15, 0.10				
5	6	7	0.4	0.08, 0.32	0.76	12	1.2	250
4	(a)	6	(a)	0.40, 0.57			1.4	269
5	5	8	Trace	0.10, 0.25	0.61	12	1.2	248
3	5	6	0.3	0.25, 0.47			1.2	278
5	8	5	(a)	0.11, 0.01	1.52	10	None	212
5	8	5	0.2	(0.19, 0.20)			1.2	261
5	7	6	0.4	-0.08, 0.30	0.74	10	2.8	219
5	8	8	0.2	(0.41, 0.58)			6	262
5	6	7	0.1	0.25, 0.30	0.57	12	1.2	328
6	7	8	Trace	0.18, 0.23			1.2	329
5	6	7	0.1	0.32, 0.34	2.3	6	1.1	327
5	6	8	Trace	0.23, 0.48			1.3	332
4	5	6	0.5	-0.05, -0.05	0.63	12	1.5	221
5	6	8	0.4	0.40, 0.28			1.1	258
5	7	7	0.4	0.07, 0.34	0.22	12	1.2	254
6	7	6	0.1	0.23, 0.28			1.2	280
6	7	7	0.1	0.30, 0.30	0.50	12	1.1	313
6	7	6	0.1	0.17, 0.17			1.1	315
6	6	6	0.1	-0.26	~1	5	1.1	314
6	6	7	Trace	0.00, 0.03			None	316
5	8	7	0.3	0.43, 0.39	0.0	12	1.3	268
6	6	8	0.3	-0.08, 0.11			1.2	273
6	7	7	0.1	0.14	1.86	11	None	310
5	6	7	0.1	-0.02, 0.08			1.1	311
6	7	8	0.1	0.00, 0.11	0.25	6	1.1	309
5	6	7	0.1	0.15, 0.30			1.1	312
6	6	9	0.3	-0.02, -0.02	0.27	12	1.2	244
7	7	6	0.2	0.36, 0.42			1.2	252
6	7	8	0.1	0.20, 0.15	0.12	12	1.1	306
6	6	7	Trace	0.17, 0.30			1.1	308
6	9	8	0.1	0.06, 0.28	0.17	6	1.1	305
6	6	6	0.1	-0.04, 0.18			1.1	307

Test Solvent	Initial Concentration (ppm)	Background Mix No.	Initial NO_x NO (ppm)	Initial NO_x NO_2 (ppm)	NO_2 Half-Life (min)	NO_2 Dosage After 4 Hrs (ppm·hr)	NO_2 Dosage After 7 Hrs (ppm·hr)	Ozone Maximum (ppm)
None	0.00	1	0.19	0.89	168	2.6	3.0	0.26
	0.00	1	0.03	1.10	174	3.0	3.5	0.30
	0.00	1	0.05	1.12	141	2.8	3.3	0.29
	0.00	1	0.08	0.90	159	2.6	3.0	0.29
	0.00	1	0.10	0.86	165	2.1	2.5	0.29
	0.00	2	0.08	0.41	120	0.9	1.0	0.21
	0.00	2	0.07	0.47	102	0.9	1.0	0.22
n-Butyl acetate	8.0	1	0.04	1.00	135	2.1	2.4	0.37
	8.0	1	0.10	1.02	147	2.4	2.8	0.34
Isobutyl acetate	8.0	1	0.04	0.87	105	2.2	2.6	0.42
	8.0	1	0.08	1.05	117	2.2	2.6	0.40
	4.0	1	0.03	1.14	141	2.7	3.2	0.38
	4.0	1	0.05	1.06	129	2.4	2.8	0.35
	4.0	2	0.11	0.36	106	1.0	1.1	0.28
	4.0	2	0.04	0.52	78	0.9	1.1	0.30
Sec. butyl acetate	8.0	1	0.10	0.89	138	2.1	2.4	0.37
	8.0	1	0.05	0.99	117	2.2	2.5	0.52
	8.0	1	0.07	0.94	114	2.1	2.3	0.40
	4.0	1	0.03	1.21	159	3.1	3.8	0.35
	4.0	1	0.24	0.87	138	2.2	2.6	0.34
	4.0	2	0.06	0.42	99	1.0	1.2	0.27
	4.0	2	0.04	0.62	108	1.3	1.5	0.27
Ethyl acetate	8.0	1	0.07	0.94	207	2.7	3.4	0.30
	8.0	1	0.04	1.14	198	3.2	4.1	0.28
Diethyl cellosolve	8.0	1	0.02	1.40	52	1.5	1.5	0.38
	8.0	1	0.04	0.93	69	0.8	0.9	0.42
	4.0	1	0.06	1.05	96	1.9	2.0	0.45
	4.0	1	0.13	0.88	87	1.4	1.5	0.40
	4.0	2	0.09	0.38	93	0.7	0.8	0.28
	4.0	2	0.08	0.41	105	0.8	0.9	0.28
Cellosolve acetate	8.0	1	0.03	1.00	108	2.0	2.2	0.48
	8.0	1	0.07	0.97	108	1.9	2.1	0.46
	4.0	1	0.13	1.05	114	2.2	2.5	0.40
	4.0	1	0.08	1.02	122	1.8	2.3	0.42
	4.0	2	0.08	0.40	132	0.9	1.1	0.29
	4.0	2	0.10	0.34	129	0.8	1.0	0.28

Note: Background Mix No. 1 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and NO_2 (1.
Background Mix No. 2 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and NO_2 (0.

a. Experimental difficulties prevented measurement.

r 7 Hrs ·hr)	Ozone Maximum (ppm)	Oxidant Dosage Maximum (ppm)	Oxidant Dosage After 4 Hrs (ppm·hr)	Oxidant Dosage After 7 Hrs (ppm·hr)	Hydrocarbon Disappearance Rate Propylene (%/hr)	Butane (%/hr)	Toluene (%/hr)	Test Solvent (%/hr)	PAN Dosage After 7 Hrs (ppm·hr)	Indi
3.0	0.26	0.29	0.6	1.5	35	7	9	None	0.8	0.20
3.5	0.30	0.33	0.7	1.6	30	5	5	None	0.4	0.24
3.3	0.29	0.33	0.7	1.6	30	5	6	None	0.3	0.19
3.0	0.29	0.31	0.8	1.7	32	7	7	None	0.3	0.40
2.5	0.29	0.32	0.8	1.7	35	6	8	None	0.2	-0.07
1.0	0.21	0.21	0.7	1.1	40	5	7	None	0.1	0.00
1.0	0.22	0.23	0.7	1.1	35	6	7	None	0.2	0.15
2.4	0.37	0.42	1.1	2.2	30	5	9	8	0.2	-0.10
2.8	0.34	0.40	1.1	2.1	38	5	7	6	0.3	0.17
2.6	0.42	0.48	1.4	2.6	37	5	7	6	0.3	-0.17
2.6	0.40	0.48	1.5	2.6	37	5	6	6	Trace	0.26
3.2	0.38	0.43	1.1	2.3	36	5	6	8	Trace	0.23
2.8	0.35	0.39	1.1	2.1	34	6	6	6	0.1	0.23
1.1	0.28	0.31	0.9	1.7	34	5	6	7	0.1	0.04
1.1	0.30	0.33	1.0	1.8	36	6	7	7	0.1	0.23
2.4	0.37	0.39	1.1	2.1	38	5	5	5	Trace	0.4
2.5	0.52	0.58	1.8	3.3	38	6	6	6	Trace	-0.1
2.3	0.40	0.44	1.4	2.5	40	6	6	6	0.1	0.2
3.8	0.35	0.39	1.1	2.1	35	6	7	7	0.1	0.3
2.6	0.34	0.37	1.1	2.0	40	6	6	7	0.1	0.2
1.2	0.27	0.29	1.0	1.7	42	5	6	6	0.1	0.3
1.5	0.27	0.30	1.0	1.7	38	5	6	6	0.1	-0.0
3.4	0.30	0.32	0.8	1.8	26	6	8	6	0.3	0.3
4.1	0.28	0.32	0.6	1.5	30	5	7	5	0.3	0.3
1.5	0.38	0.49	1.5	2.2	42	5	5	7	(a)	0.3
0.9	0.42	0.64	1.9	3.0	(a)	5	3	9	(a)	0.
2.0	0.45	0.58	1.7	2.9	46	6	5	10	0.1	0.
1.5	0.40	0.51	1.7	2.7	43	6	6	9	0.1	0.
0.8	0.28	0.35	1.1	1.9	43	5	6	9	0.1	0.
0.9	0.28	0.36	1.2	2.1	44	5	6	8	0.1	0.
2.2	0.48	0.54	1.7	2.8	37	5	7	9	(a)	0.
2.1	0.44	0.53	1.7	2.8	26	4	7	7	0.3	0.
2.5	0.40	0.49	1.4	2.7	45	4	6	9	0.1	0.
2.3	0.42	0.52	1.6	2.8	32	5	6	9	0.1	0.
1.1	0.29	0.34	1.1	1.8	38	6	7	9	Trace	0.
1.0	0.28	0.34	1.0	1.9	45	5	5	9	0.1	0.

m), and NO_2 (1.0 ppm).

m), and NO_2 (0.5 ppm).

B

Table 3

IRRADIATION EXPERIMENTS WITH STANDARD BACKGROUND MIXES AND ESTER AND ETHER SOLVENTS

Disappearance Rate		PAN Dosage	Eye Irritation			Maximum	Run
Toluene (%/hr)	Test Solvent (%/hr)	After 7 Hrs (ppm·hr)	Indices	Statistical Comparison: Solvent vs Background Mix t	df	Aerosol (air=1)	Number
						2.1	1
9	None	0.8	0.20, 0.16			1.6	214
5	None	0.4	0.24, 0.08			1.8	222
6	None	0.3	0.19, 0.25			1.4	267
7	None	0.3	0.40, 0.54			1.2	289
8	None	0.2	-0.07, 0.08			1.1	317
7	None	0.1	0.00, 0.20			1.1	318
7	None	0.2	0.15, 0.10				
9	8	0.2	-0.10, 0.23	1.02	12	1.1	243
7	6	0.3	0.17, 0.15			1.1	288
7	6	0.3	-0.17, -0.02	1.45	12	1.2	213
6	6	Trace	0.20, 0.22			1.5	279
6	8	Trace	0.22, 0.30	1.25	12	1.1	320
6	6	0.1	0.23, 0.25			1.1	331
6	7	0.1	0.04	0.83	5	1.1	321
7	7	0.1	0.25, 0.34			1.1	322
5	5	Trace	0.41, 0.44	1.52	12	1.5	202
6	6	Trace	-0.14, 0.10			1.4	233
6	6	0.1	0.27, 0.27	1.00	13	1.1	290
7	7	0.1	0.36, 0.28			1.1	324
6	7	0.1	0.20			1.1	326
6	6	0.1	0.30, 0.32	0.69	6	1.1	323
6	6	0.1	-0.04, 0.20			1.1	325
8	6	0.3	0.30, 0.20	0.78	12	1.4	247
7	5	0.3	0.30, 0.34			1.3	257
5	7	(a)	0.38, 0.19	0.0	12	3.9	201
3	9	(a)	0.11, 0.17			2.2	232
5	10	0.1	0.23	0.33	11	2.1	301
6	9	0.1	0.22, 0.19			2.2	302
6	9	0.1	0.14, 0.18	0.43	5	1.4	303
6	8	0.1	0.09			1.4	304
7	9	(a)	0.26, 0.15	0.34	12	1.5	234
7	7	0.3	0.13, 0.16			1.2	277
6	9	0.1	0.05, 0.05	0.43	11	1.3	297
6	9	0.1	0.32			1.7	299
7	9	Trace	0.19, 0.23	0.33	6	1.2	298
5	9	0.1	0.02, 0.11			1.4	300

Test Solvent	Initial Concentration (ppm)	Background Mix No.	Initial NO_x NO (ppm)	Initial NO_x NO_2 (ppm)	NO_2 Half-Life (min)	NO_2 Dosage After 4 Hrs (ppm·hr)	NO_2 Dosage After 7 H (ppm·hr)
None	0.00	1	0.19	0.89	168	2.6	3.0
	0.00	1	0.03	1.10	174	3.0	3.5
	0.00	1	0.05	1.12	141	2.8	3.3
	0.00	1	0.08	0.90	159	2.6	3.0
	0.00	1	0.10	0.86	165	2.1	2.5
	0.00	2	0.08	0.41	120	0.9	1.0
	0.00	2	0.07	0.47	102	0.9	1.0
Toluene	8.0[a]	1	0.07	0.89	72	1.4	1.6
	8.0[a]	1	0.10	0.95	102	1.7	1.8
	4.0[a]	1	0.03	1.10	117	2.2	2.4
	4.0[a]	1	0.03	1.12	107	2.3	2.5
	4.0[a]	2	0.08	0.54	54	0.7	0.8
	4.0[a]	2	0.06	0.48	78	0.4	0.9
Nonane	8.0	1	0.01	1.10	112	2.4	2.7
	8.0	1	0.07	1.06	117	2.1	2.5
2-Nitropropane	8.0	1	0.06	1.00	141	3.2	3.8
	8.0	1	0.07	1.03	120	2.0	2.4
1,1,2-Trichloroethane	8.0	1	0.02	1.14	159	2.9	3.5
	8.0	1	0.04	1.08	174	2.7	3.2
Methylene chloride	8.0	1	0.01	1.14	192	3.2	3.9
	8.0	1	0.07	1.03	144	2.5	3.0
Freon 113	8.0	1	0.06	1.06	138	2.6	2.9
	8.0	1	0.04	0.96	189	2.6	3.2

Notes: Background Mix No. 1 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and N
Background Mix No. 2 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and N

a. In addition to the 1 ppm added with the background mix.
b. See values given under Toluene (immediately left).
c. Experimental difficulties prevented measurement.

Dosage		Ozone	Oxidant		Hydrocarbon Disappearance Rate				PAN
			Dosage						
rs	After 7 Hrs (ppm·hr)	Maximum (ppm)	Maximum (ppm)	After 4 Hrs (ppm·hr)	After 7 Hrs (ppm·hr)	Propylene (%/hr)	Butane (%/hr)	Toluene (%/hr)	Test Solvent (%/hr)	Aft (p
	3.0	0.26	0.29	0.6	1.5	35	7	9	None	
	3.5	0.30	0.33	0.7	1.6	30	5	5	None	
	3.3	0.29	0.33	0.7	1.6	30	5	6	None	
	3.0	0.29	0.31	0.8	1.7	32	7	7	None	
	2.5	0.29	0.32	0.8	1.7	35	6	8	None	
	1.0	0.21	0.21	0.7	1.1	40	5	7	None	
	1.0	0.22	0.23	0.7	1.1	35	6	7	None	
	1.6	0.23	0.24	0.7	0.9	33	5	7	(b)	
	1.8	0.24	0.24	0.6	0.9	45	7	6	(b)	
	2.4	0.26	0.28	0.8	1.3	35	6	7	(b)	
	2.5	0.25	0.28	0.8	1.3	36	6	7	(b)	
	0.8	0.19	0.19	0.5	0.8	38	6	6	(b)	
	0.9	0.19	0.19	0.6	0.8	42	6	7	(b)	
	2.7	0.44	0.51	1.2	2.4	34	5	7	7	
	2.5	0.38	0.46	1.3	2.4	36	6	5	6	
	3.8	0.38	0.41	1.2	2.3	35	6	7	6	
	2.4	0.34	0.38	1.1	2.2	42	6	6	6	
	3.5	0.34	0.38	0.7	1.8	28	6	(c)	6	
	3.2	0.30	0.34	0.8	1.8	40	6	(c)	6	
	3.9	0.28	0.31	0.7	1.6	32	6	8	5	
	3.0	0.30	0.31	0.8	1.7	37	6	8	5	
	2.9	0.34	0.38	0.7	1.8	38	8	9	4	
	3.2	0.30	0.34	0.8	1.7	32	5	7	5	

(1.0 ppm), and NO_2 (1.0 ppm).

(1.0 ppm), and NO_2 (0.5 ppm).

Table 4

IRRADIATION EXPERIMENTS WITH STANDARD BACKGROUND MIXES AND MISCELLANEOUS SOLVENTS

e Rate est Solvent (%/hr)	PAN Dosage After 7 Hrs (ppm·hr)	Eye Irritation Indices	Eye Irritation Statistical Comparison: Solvent vs Background Mix t	df	Maximum Aerosol (air=1)	Run Number
					2.1	i
None	0.8	0.20, 0.16			1.6	214
None	0.4	0.24, 0.08			1.8	222
None	0.3	0.19, 0.25			1.4	267
None	0.3	0.40, 0.54			1.2	289
None	0.2	-0.07, 0.08			1.1	317
None	0.1	0.00, 0.00			1.1	318
None	0.2	0.15, 0.10				
(b)	None	-0.18, -0.15	1.26	12	7.3	211
(b)	0.2	0.18, 0.38			7.5	283
(b)	0.1	0.01, 0.34	0.21	12	5.8	294
(b)	0.2	0.10, 0.14			6.2	295
(b)	0.1	-0.04, 0.16	0.72	6	2.5	296
(b)	0.2	0.40, 0.40			1.6	319
7	Trace	0.15, 0.13	0.32	12	1.3	249
6	0.1	0.32, 0.38			1.3	259
6	(c)	0.26, 0.40	0.10	12	1.9	246
6	0.3	0.03, 0.17			1.4	287
6	0.5	0.15, -0.02	1.64	12	1.4	216
6	Trace	0.00, 0.10			1.6	272
5	0.2	0.38, 0.34	0.42	12	1.3	253
5	0.2	0.20, 0.08			1.5	285
4	(c)	0.05, 0.04	0.27	12	1.7	217
5	(c)	0.43, 0.45			1.6	256

Table 5

EFFECT OF SOLVENT CONCENTRATION ON BACKGROUND MIX

Test Solvent	Initial Concentration (ppm)	Nitrogen Dioxide Half-Life (min)	Nitrogen Dioxide Dosage After 7 Hrs (ppm·hr)	Oxidant Maximum Concentration (ppm)	Oxidant Dosage After 7 Hrs (ppm·hr)	Comments
Background mix only	--	161 ± 13	3.1 ± 0.4	0.32 ± 0.02	1.6 ± 0.1	
Cyclohexanone	8	195 ± 9	4.0 ± 0.1	0.33 ± 0.02	1.6 ± 0.1	Aerosol 2.8 - 6 units
Cyclohexanone	4	191 ± 13	3.6 ± 0.1	0.29 ± 0.01	1.3 ± 0.1	Aerosol insignificant
Isopropyl alcohol	8	110 ± 5	2.3 ± 0.1	0.42 ± 0.01	2.2 ± 0.1	
Isopropyl alcohol	4	134 ± 2	2.5 ± 0.1	0.38 ± 0.01	2.0 ± 0.1	
Isobutyl alcohol	8	128 ± 8	2.2 ± 0.1	0.41 ± 0.01	2.1 ± 0.1	
Isobutyl alcohol	4	75 ± 12	1.9 ± 0.1	0.40 ± 0.01	2.1 ± 0.1	
n-Butyl alcohol	8	99 ± 1	1.9 ± 0.2	0.40 ± 0.01	2.1 ± 0.1	
n-Butyl alcohol	4	132 ± 12	2.6 ± 0.1	0.39 ± 0.01	2.0 ± 0.1	
Isobutyl acetate	8	111 ± 6	2.6 ± 0.1	0.48 ± 0.01	2.6 ± 0.1	
Isobutyl acetate	4	135 ± 6	3.0 ± 0.2	0.41 ± 0.02	2.2 ± 0.1	
Sec. butyl acetate	8	123 ± 13	2.4 ± 0.1	0.47 ± 0.10	2.6 ± 0.6	
Sec. butyl acetate	4	149 ± 11	3.2 ± 0.6	0.38 ± 0.01	2.1 ± 0.1	
Diethyl cellosolve	8	61 ± 9	1.2 ± 0.3	0.57 ± 0.08	2.6 ± 0.4	
Diethyl cellosolve	4	92 ± 5	1.8 ± 0.3	0.55 ± 0.04	2.8 ± 0.1	
Cellosolve acetate	8	108 ± 1	2.2 ± 0.1	0.54 ± 0.01	2.8 ± 0.1	
Cellosolve acetate	4	118 ± 4	2.4 ± 0.1	0.51 ± 0.02	2.8 ± 0.1	
Toluene	8	87 ± 15	1.7 ± 0.1	0.24 ± 0.01	0.9 ± 0.1	Aerosol 7.3 - 7.5 units
Toluene	4	112 ± 5	2.5 ± 0.1	0.28 ± 0.01	1.3 ± 0.1	Aerosol 6.2 - 5.8 units

Table 6

EFFECT OF SOLVENT (4 ppm) ON DIFFERENT BACKGROUND MIXES

Test Solvent	Background Mix	Half-Life (min)	Dosage After 7 Hrs (ppm·hr)	Maximum Concentration (ppm)	Dosage After 7 Hrs (ppm·hr)	Comments
None	1	161 ± 13	3.1 ± 0.1	0.32 ± 0.02	1.6 ± 0.1	
None	2	111 ± 9	1.0 ± 0.1	0.22 ± 0.01	1.1 ± 0.1	
Cyclohexanone	1	191 ± 13	3.6 ± 0.1	0.29 ± 0.01	1.3 ± 0.1	
Cyclohexanone	2	174 ± 18	1.4 ± 0.2	0.22 ± 0.01	1.1 ± 0.1	
Isopropyl alcohol	1	134 ± 2	2.5 ± 0.1	0.38 ± 0.01	2.0 ± 0.1	
Isopropyl alcohol	2	101 ± 8	1.0 ± 0.2	0.28 ± 0.01	1.4 ± 0.2	
Isobutyl alcohol	1	75 ± 12	1.9 ± 0.1	0.40 ± 0.01	2.1 ± 0.1	
Isobutyl alcohol	2	99 ± 27	1.1 ± 0.3	0.29 ± 0.01	1.6 ± 0.1	
n-Butyl alcohol	1	132 ± 12	2.6 ± 0.1	0.39 ± 0.01	2.0 ± 0.1	
n-Butyl alcohol	2	116 ± 8	1.0 ± 0.1	0.28 ± 0.01	1.6 ± 0.1	
Isobutyl acetate	1	135 ± 6	3.0 ± 0.2	0.41 ± 0.02	2.2 ± 0.1	
Isobutyl acetate	2	92 ± 14	1.1 ± 0.1	0.32 ± 0.01	1.8 ± 0.1	
Sec. butyl acetate	1	149 ± 11	3.2 ± 0.6	0.38 ± 0.01	2.1 ± 0.1	
Sec. butyl acetate	2	104 ± 5	1.4 ± 0.2	0.30 ± 0.01	1.7 ± 0.1	
Diethyl cellosolve	1	92 ± 5	1.8 ± 0.3	0.55 ± 0.04	2.8 ± 0.1	
Diethyl cellosolve	2	99 ± 6	0.9 ± 0.1	0.36 ± 0.01	2.0 ± 0.1	
Cellosolve acetate	1	118 ± 4	2.4 ± 0.1	0.51 ± 0.02	2.8 ± 0.1	
Cellosolve acetate	2	131 ± 2	1.1 ± 0.1	0.34 ± 0.01	1.9 ± 0.1	
Toluene	1	112 ± 5	2.5 ± 0.1	0.28 ± 0.01	1.3 ± 0.1	Aerosol 6.2 - 5.8 units
Toluene	2	66 ± 12	0.9 ± 0.1	0.19 ± 0.01	0.8 ± 0.1	Aerosol 2.5 - 1.6 units

Notes: Background Mix No. 1 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and NO_2 (1.0 ppm).
Background Mix No. 2 - propylene (0.5 ppm), butane (2.0 ppm), toluene (1.0 ppm), and NO_2 (0.5 ppm).

Table 7

SOLVENT REACTIVITY CATEGORY SUMMARY

Solvents	Category			
	NO_2 Half-Life (Figures 5 and 6)	Oxidant Maximum (Figures 7 and 8)	Oxidant Dosage (Figures 9 and 10)	Aerosol (Tables 2-4)
Methyl isobutyl ketone	-1	0	0	0
Methyl isoamyl ketone	-1	0	0	0
Methyl ethyl ketone	-1	0	0	0
Cyclohexanone	+1	0	-1	+1
Diacetone alcohol	-1	+1	0	0
Isopropyl alcohol	-1	+1	+1	0
Isobutyl alcohol	-1	+1	+1	0
n-Butyl alcohol	-1	+1	+1	0
n-Butyl acetate	-1	+1	0	0
Isobutyl acetate	-2	+1	+1	0
Sec. butyl acetate	-1	+1	+1	0
Ethyl acetate	+1	0	0	0
Diethyl cellosolve	-2	+2	+2	0
Cellosolve acetate	-1	+2	+2	0
Toluene	-2	-1	-2	+2
n-Nonane	-1	+1	+1	0
2-Nitropropane	-1	+1	+1	0
1,1,2-Trichloroethane	0	0	0	0
Methylene chloride	0	0	0	0
Freon 113	0	0	0	0

Table 8

WEAKEST BONDS IN TEST SOLVENTS

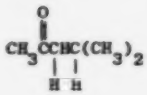
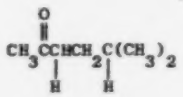
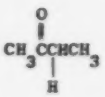
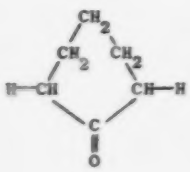
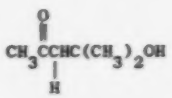
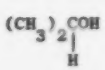
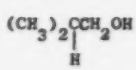
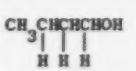
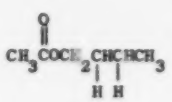
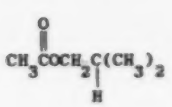
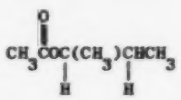
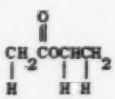
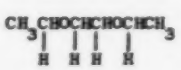
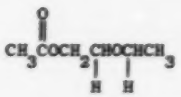
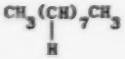
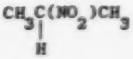
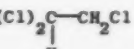
Test Solvent No.	Test Solvent Name	Weakest Bonds	Bond Dissociation Energy (kcal/mole)	% Diviation of Actual from Predicted Disappearance Rate
1.	Methyl isobutyl ketone		92	-16
2.	Methyl isoamyl ketone		92	-10
3.	Methyl ethyl ketone		92	-100
4.	Cyclohexanone		92	+31
5.	Diacetone alcohol		89	+44
6.	Isopropyl alcohol		92	+44
7.	Isobutyl alcohol		92	+56
8.	n-Butyl alcohol		95	+44
9.	n-Butyl acetate		95	+4
10.	Isobutyl acetate		92	-5

Table 8 (Concluded)

No.	Test Solvent Name	Weakest Bonds	Bond Dissociation Energy (kcal/mole)	% Deviation of Actual from Predicted Disappearance Rate
11.	Sec.butyl acetate		95	-39
12.	Ethyl acetate		98	-52
13.	Diethyl cellosolve		93	+58
14.	Cellosolve acetate		93	+92
15.	Toluene		85	Not predicted
16.	n-Nonane		95	-59
17.	2-Nitropropane		92	-15
18.	1,1,2-Trichloroethane		92	+58
19.	Methylene chloride		104	-100
20.	Freon 113	$FCCl_2CF_2Cl$	?	0

Data furnished by Dr. D. Golden, Kinetics and Thermochemistry Group, Stanford Research Institute, Menlo Park.

Appendix A

DESIGN AND PERFORMANCE OF A FACILITY (SMOG CHAMBER) FOR STUDYING PHOTOCHEMICAL REACTIONS UNDER CONDITIONS SIMULATING THE TROPOSPHERIC ATMOSPHERE

DESIGN AND PERFORMANCE OF A FACILITY (SMOG CHAMBER) FOR STUDYING PHOTOCHEMICAL REACTIONS UNDER CONDITIONS SIMULATING THE TROPOSPHERIC ATMOSPHERE

George J. Doyle

The design and construction of a facility for studying photochemical reactions in air under tropospheric conditions (photochemical smog) is described. Salient aspects of the facility are: (1) use of catalytic combustion over platinum at elevated pressures (5-8 atm) and temperatures (600°C) to remove inadvertent contaminants from air used to make up the reaction mixtures, (2) close control of humidity and temperature (down to 27°C), (3) a low exchange rate between the reaction chamber and the ambient atmosphere (1.5%/hr), (4) approximate simulation of tropospheric radiation between 300 and 600 nm, and (5) a Teflon-lined reaction chamber.

The purified air contains less than 0.5 ppm nitrogen dioxide and a trace of organic impurity that is photochemically inactive. Ozone has a long half-life, both irradiated and nonirradiated (7.8 and 20 hours) within the reaction chamber. Photooxidation of trace concentrations of olefin and nitric oxide gives results somewhat different from but comparable with those of other investigators.

Introduction

Stanford Research Institute built its first smog chamber in the late forties. That chamber was used to study eye irritation effects of various compounds found in polluted air. In 1954 a second chamber was built to study plant damage by irradiated night air in Los Angeles, and this chamber was eventually converted to a photochemical reactor for studies on auto exhaust and olefin - nitrogen oxide mixtures in purified air. Eye irritation was the principal manifestation studied in using the converted chamber. This paper describes the Institute's third-generation chamber, constructed to study the relative contribution of industrial solvents to photochemical smog. Included

here are details of the chamber's design objectives, construction, and performance as compared with that of other reaction chambers.

The participants in chemical reactions occurring in polluted tropospheric air, with the exception of oxygen, are usually present at parts per million concentrations or below. Many of these overall reactions have essential photochemical steps driven by radiation from the sun, both direct radiation and that scattered by the atmosphere (Leighton, 1961). In some cases, water vapor has been shown to affect the course of a reaction (Dimitriades, 1967). Relatively small changes of temperature have been shown to appreciably affect reaction speed for some trace compounds (Bufalini and Altshuller, 1963). These facts strongly influence the design of a smog chamber and its auxiliaries for studying reactions under simulated tropospheric conditions.

The low concentration levels of participants in chemical reactions introduce both analytical difficulties and stringent requirements on the purity of the air used to make up the reaction mixture. Humidity must be controlled. The materials of construction must be such that they do not introduce appreciable concentrations of impurities or react with components of the reaction mixture.

The radiation sources used for irradiation of the smog chamber contents should simulate the intensity and spectral distribution prevailing in the lower troposphere within spectral regions considered photochemically effective. In addition, spatial and temporal distributions within the reaction chamber must be as uniform as practicable.

The temperature of the chamber must be controlled to within a few degrees. Closer control is not needed because the changes of reaction rate with temperature are not large (Bufalini and Altshuller, 1963) and because the lack of precision of most analytical methods at trace concentrations would make more precise temperature control useless.

The reaction chamber must be large for several reasons. An intrinsic reason is the need to make homogenous reactions the dominant type of reaction, as it is under tropospheric conditions. Simple considerations on the competition between radical termination at the walls and radical-radical reaction (Noyes, 1960) suggest a volume on the order of cubic meters at sub part-per-million levels of a typical radical-producing photoacceptor. Analytical procedures at part-per-million concentration levels usually require a sample ranging upward from a few liters, and destructive sampling must consume a small fraction of reaction chamber contents. In some instances it is also desirable to evaluate the severity of some typical manifestation of photochemical smog using

the reaction mixture. In the chamber described here, the manifestation being studied is eye irritation. This requires that at some stage of the reaction the several members of a panel simultaneously expose their eyes to the chamber's contents and evaluate the severity of irritation. Such measurements dictate a chamber large enough to accommodate these persons and to minimize the effect on the chamber's contents of the exposure of tissue.

Since the discovery that photochemical reactions play a major role in producing undesirable compounds in the atmosphere (Haagen-Smit, Bradley, et al., 1952), several chambers have been built for use in studying and evaluating the pollution potential resulting from reaction of various compounds and mixtures of compounds. Some of these chambers were designed and built for the same purposes as the chamber described here (Brunelle, Dickenson, et al., 1966; Hamming and Lausche, 1963; Schuck, 1957). The SRI chamber was designed on the basis of our own and others' experience, keeping the shortcomings of previous chambers in mind. The major troubles encountered in previous chambers are (1) an appreciable and variable level of contamination in air used to make up the reaction mixture, (2) an undesirably high rate of exchange between the chamber and the ambient atmosphere, (3) the use of construction materials having surfaces of dubious passivity for typical products of the reaction, (4) inability to maintain the temperature of chamber contents at a level representative of tropospheric temperatures, (5) irradiation with sources that do not simulate photochemically effective tropospheric radiation in spectral distribution or intensity, and (6) irradiation with sources that are not spatially uniform.

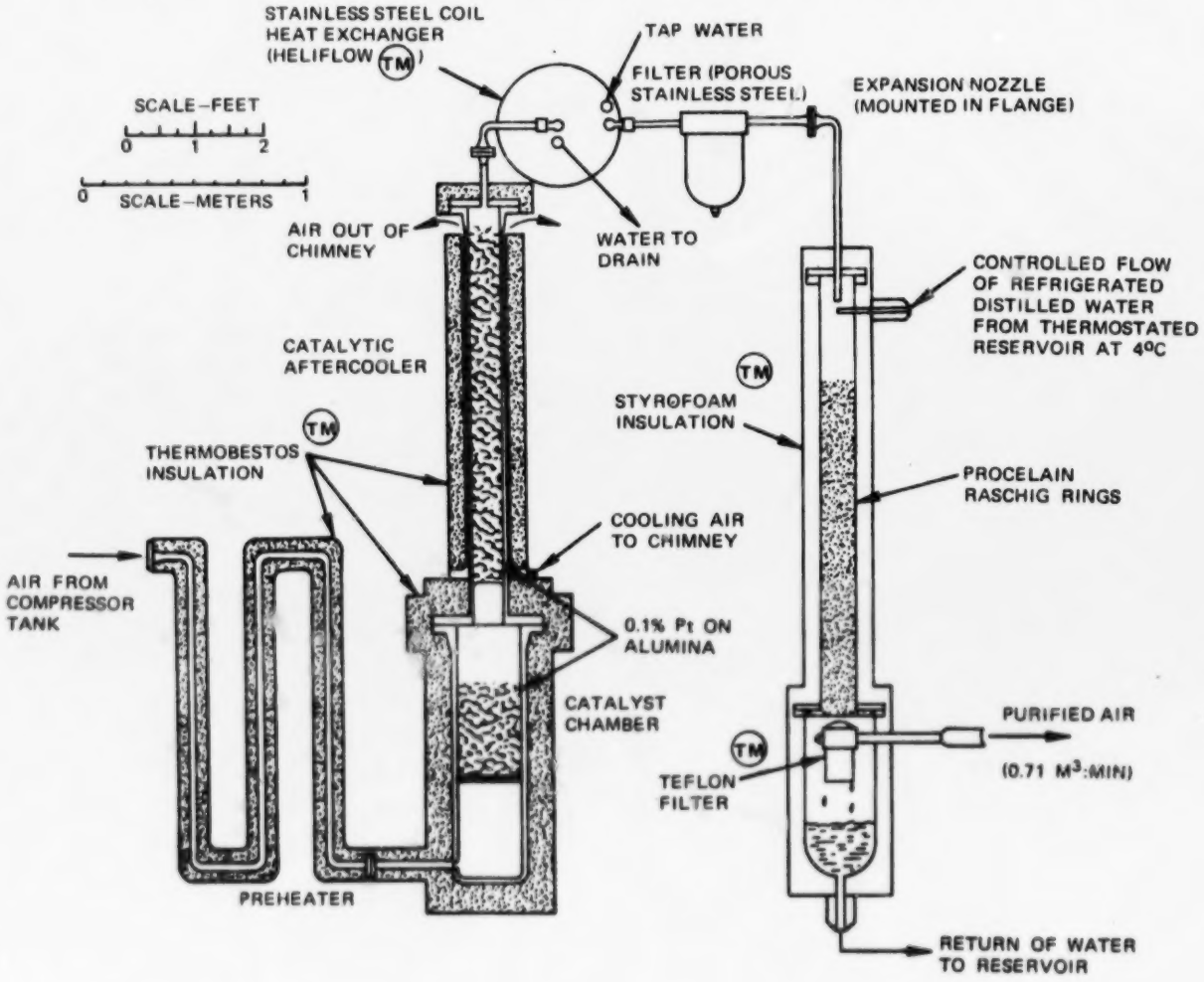
Although many of these shortcomings are the result of budgetary constraints, the SRI chamber was designed to mitigate them to the extent possible, still within budgetary constraints. For example, contamination of the air is reduced by catalytic combustion. Chamber exchange rate is reduced by the use of O-ring seals for chamber panels and by temperature control, which reduces breathing effects. Interior surfaces are mainly Pyrex glass and aluminum covered with fused Teflon films, to increase surface passivity. A mixture of fluorescent lamp types enclose the chamber as a radiant shell to simulate solar radiation from 300 to 600 nm and to attain an approximately uniform absorption rate throughout the chamber, both spatial and temperal.

Chamber Design

Air Purification System. The air purification system is shown semischematically in Figure 1. Specially constructed items are drawn to scale. Commercially available items are shown schematically. Considerable detail, such as studs, bolts, heaters, thermocouple wells, pumps, and reservoirs, has been

Figure 1

AIR PURIFICATION SYSTEM FOR SRI SMOG CHAMBER



Reproduced from best available copy.

omitted for clarity. Flange gaskets in high temperature portions of the system consist of a thin cross-section of a helical laminate of alternative layers of stabilized stainless steel foil and mica trapped inside a carbon steel ring (such as Flexitallic "ceramic" gaskets). Such gaskets do not contaminate the purified air and, in addition, are usable at temperatures near 600°C.

The organic content of the air was reduced to negligible amounts by catalytic oxidation. This method had been used with considerable success with a previous SRI chamber (Schuck, 1957). A compromise was made (partly on the basis of cost) between complete removal of organic materials and catalytic formation of nitrogen oxides.

The catalyst chamber and preheater were designed to handle 0.71 m^3/min (1 atm, 25°C) of air. This flow rate allows a minimum residence time in the chamber of approximately ten minutes. Ambient air is first compressed by a single-stage, water-cooled, nonlubricated compressor. This allows partial dehumidification to facilitate a later simple humidification step and increases the absolute concentration of oxygen and contaminant over the catalyst to cause increased oxidation rates. The air is fed through a zigzag section of Schedule 40, 2.54-cm stainless steel pipe (columbium- or titanium-stabilized austenitic, AISI Types 321 or 347) electrically heated to 650°C. The length of the pipe (about 4.9m) was chosen on the basis of Nusselt's heat exchange data (Nusselt, 1909) as presented by McAdams in a nomograph (McAdams, 1960). Six Inconel-clad 9.5-mm tubular heaters are strapped and cemented in pairs to the exterior of each of three joined L sections of the preheater zigzag. A special heat-conducting cement was used. These heaters can furnish up to 12.6 kw of heat flux. One set of three heaters are used for sustaining heat; they derive power from 240-volt, 3-phase, 60-Hz mains. The other set of three operates with variable, autotransformer-reduced, 3-phase voltage modulated by a variable duty cycle temperature controller that maintains exit air at 600°C. The control sensor is a thermocouple in a well inserted into the exit air. A second thermocouple in a well welded to the pipe at the exit serves as a sensor for an excess temperature shutdown system. The entire system is insulated with Johns-Manville Thermobestos.

Exit air from the preheater is injected into a catalyst chamber by means of a welded side arm below a heavy screen supporting 0.0283 m^3 (1 ft^3) of platinized (0.1%) alumina pellets (3.2 x 3.2 mm) within a section of 30.5-cm, Schedule 40, stabilized stainless steel pipe. This section is terminated at one end with a welded cap and at the other with a bolt flange welded to the pipe. The assembly is supported on a tripod welded to the pipe near the bolt flange. The entire assembly is held at a preset temperature (nominally 600°C) by six 2-kw heater bands (Chromalox HBT-120) arranged in circuitry very similar to that of the

preheater, except that both sustaining power and controlling heater power are set by variable autotransformers. This assembly is also heavily insulated.

Catalyst volume was chosen on the basis of previous SRI experience (Schuck, 1957). Since pressure in the current purifier is higher than in the one used by Schuck, this purifier is probably more efficient. There are few data in the periodical literature on the efficiency of catalytic oxidizers under these conditions. A partial exception is a paper by R. H. Jones (1966), who studied 0.5% palladium on 3.2 x 3.2-mm alumina pellets at 260°C as a catalyst for oxidizing 1,000 ppm of methane in air. Extrapolation from these data suggests a 0.5% palladium catalyst volume of around 0.71 m^3 for a flow rate of 0.71 m^3/min to reduce methane fiftyfold under his conditions.

Platinum catalysts are known to be effective in catalyzing the reaction

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (1)$$

Probably the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2 \qquad (2)$$

is also catalyzed. Nitrogen oxides are undesirable in the air supply to a smog chamber because they are often one of the added trace reactants used in the studies. Figure 2 shows thermodynamically calculated equilibrium concentrations of these oxides in air at various temperatures at a total pressure of 8 atm, and Table 1 gives the equilibrium constants used to obtain data in Figure 2. The perfect gas approximation was used to calculate fugacities. Thermodynamic data were taken from Lewis and Randall (1961) as revised by Pitzer and Brewer. Figure 2 shows that at 600°C the total oxides at equilibrium will amount to 12.7 ppm (58% nitric oxide, 42% nitrogen dioxide). To avoid quenching the reaction mixture near this concentration, it is passed through a catalytic aftercooler before it enters the heat exchanger. The catalytic aftercooler consists of a section of 15.2-cm, Schedule 40, stainless steel pipe containing an additional 0.0283 m^3 of catalyst and bolted to the top of the catalyst chamber by a reducing flange joint. The aftercooler is cooled by a cocurrent stream of ambient air blown through an externally insulated coaxial chimney around the 15.2-cm pipe. The purpose of the cocurrent flow of coolant is to drop the bed temperature close to the entrance toward the exit temperature, so that maximum residence time is allowed for equilibration near and at the exit temperature.

Figure 2

EQUILIBRIUM CONCENTRATIONS OF NITROGEN OXIDES IN AIR AT 8 ATM AND VARYING TEMPERATURES

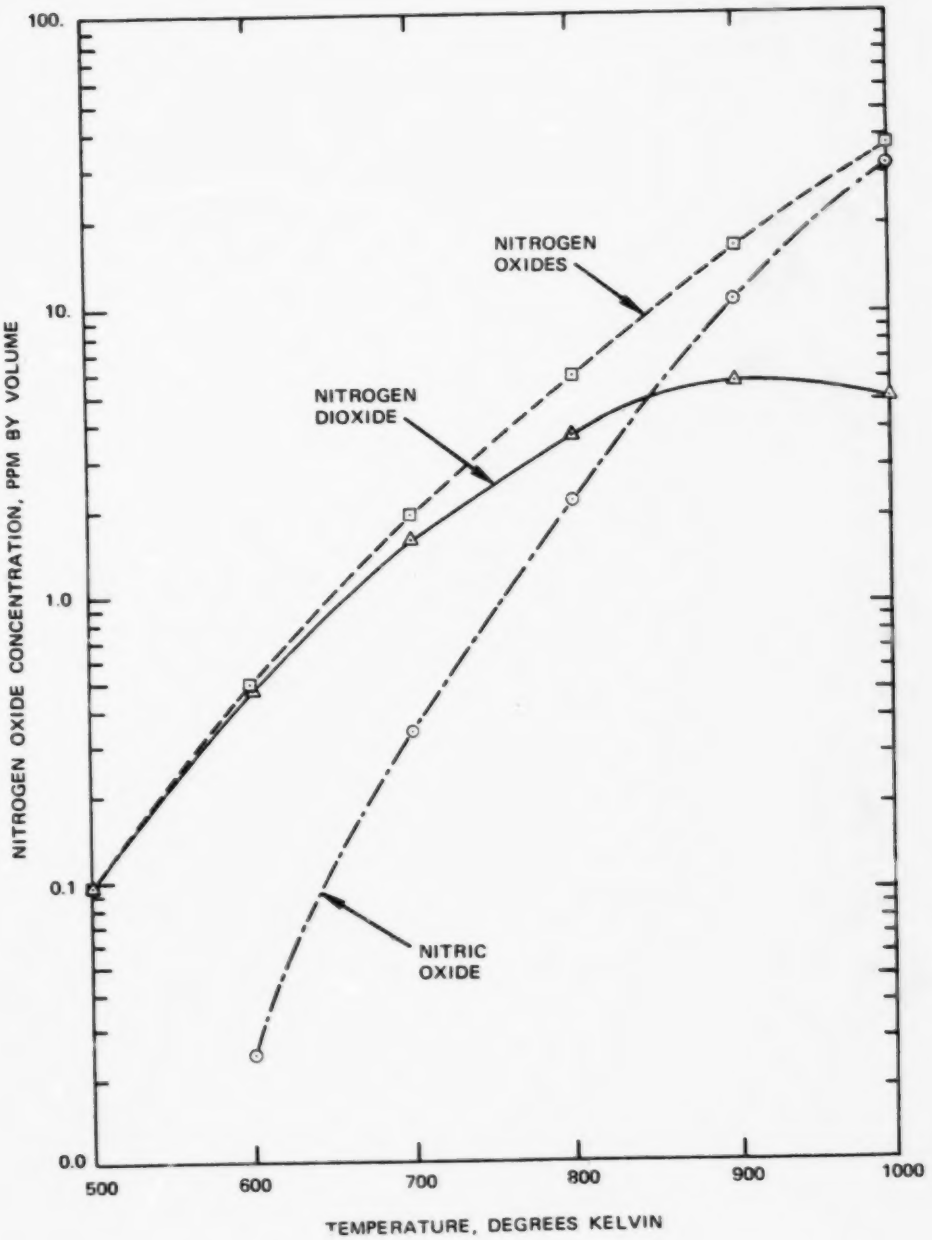


Table 1

EQUILIBRIUM CONSTANTS USED TO CALCULATE
NITROGEN OXIDE CONCENTRATIONS AT 8 ATMOSPHERES

Temperature (^{o}K)	K_1 (dimensionless)	K_2 (atm^{-1})
500	2.52×10^{-18}	3.54×10^{-14}
600	3.72×10^{-15}	8.75×10^{-13}
700	7.25×10^{-13}	1.00×10^{-11}
800	3.04×10^{-11}	5.25×10^{-11}
[illegible]00	7.59×10^{-10}	1.29×10^{-10}
1000	7.09×10^{-9}	1.00×10^{-10}

The design objective was a residual concentration of nitrogen oxides of 0.5 ppm or less at the output of the aftercooler. Assuming near equilibration, this objective would require an exit temperature near or below 327°C (Figure 2). At this temperature, the equilibrium concentration, 0.5 ppm nitrogen oxide, would contain 96% nitrogen dioxide. Being more chemically active than nitric oxide, nitrogen dioxide might be removed by a bed of pellets containing one of several metal oxides (e.g., lead dioxide). This measure was not taken because the SRI chamber could tolerate sub part-per-million levels in the first series of experiments. In addition, the efficiency of such a bed is not known at sub part-per-million levels.

Exit air from the aftercooler enters a commercial, water-cooled heat exchanger (Heliflow) and is cooled so that on expansion of the air from the exchanger to near 1 atm pressure it will attain a temperature at or slightly above 30°C. It is then filtered and expanded through a critical orifice to limit the flow to 0.71 m^3/min. At this point the air pressure is slightly more than 1 atm and at a temperature near 30°C. Its water content corresponds roughly to 10% relative humidity at ambient conditions.

To rehumidify the air to a desired humidity (nominally 35% at 1 atm and 25°C), it is passed cocurrently with a regulated stream of refrigerated distilled water (4°C) through an insulated 1.52-m by 15.2-cm-diameter column of porcelain Raschig rings (25.4 x 25.4 x 3.2 mm). This column has a calculated

height of 2.3 HEMTU (height equivalent to mass transfer unit) under these conditions. The temperature at the bottom of the bed is then essentially equal to the dew point of the exit air. A thermistor thermometer at this point is used as a sensor to control the flow rate of cold, distilled water, thus holding this temperature to a preset value. A porous Teflon filter, shielded from direct contact with the water draining from the bottom of the column, is used to filter the air before it exits from the humidifying tower.

Air Flow Control and Mixing System. Because the photochemical reaction chamber was to be used as a stirred static reactor and as a stirred flow reactor, provision had to be made for a continuous flow of reaction mixture to the chamber. Streams of purified air and of one or more trace constituents prediluted with nitrogen are metered to venturi mixers before delivery to the chamber. The Reynolds' number within the elongated throats of these mixers ranges from 3,100 to 15,500, thus ensuring turbulence.

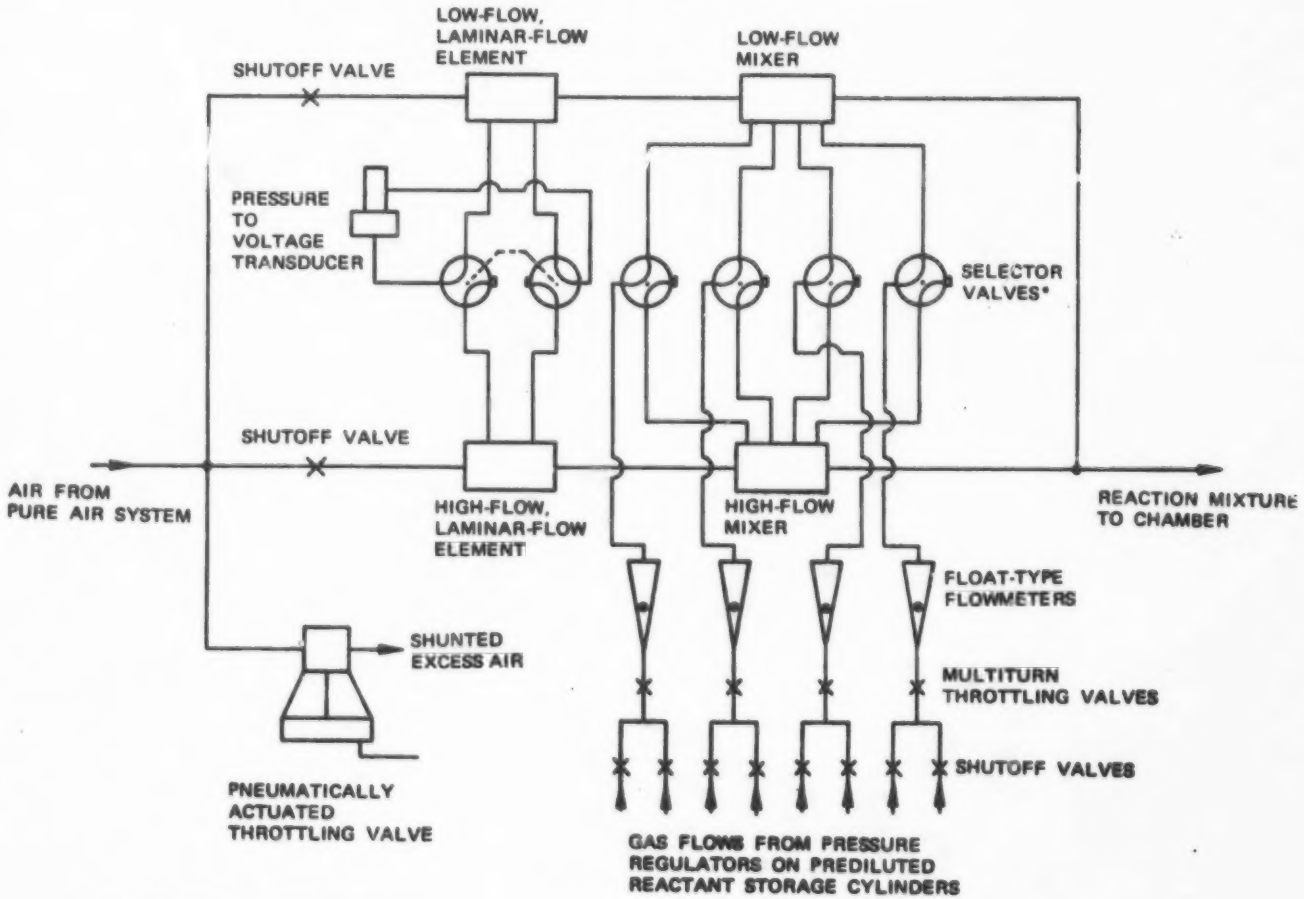
Two mixers and two laminar flow elements, one for each flow range, are used to avoid excessive pressure drops at extreme flows. One mixer covers 0.00283 to 0.0354 m^3/min (3.2 mm-diameter throat) and the other 0.0354 to 0.71 m^3/min (15.9-mm-diameter throat). Air is metered into these mixers through the laminar flow units. Pressure drops across either of these units can be applied to a strain gauge type of pressure transducer. The output of the strain gauge bridge is used in a hybrid electropneumatic feedback loop to maintain a preset flow by shunt regulation. Shunted excess purified air is discarded to the atmosphere by means of a pneumatically activated valve. Prediluted reagents (stored in 2,000-psig cylinders equipped with special noncontaminating pressure regulators) are presented to a shutoff valve and a micrometer valve in series. Flow from the micrometer valve passes through a float-type flowmeter to one of the venturi mixers. This system is shown schematically in Figure 3. Materials of construction are stainless steel, Teflon, Viton, and glass. Exceptions to use of these materials occur in the pneumatically actuated valve and in the high-flow, laminar-flow element. The latter has an aluminum case and a passivated, carbon steel, flow resistance element mounted in a polyvinyl chloride support. The accessible range of reaction chamber residence times with this system is 10.8 to 2,600 minutes (chamber volume 7.65 m^3).

Photochemical Reaction Chamber

Construction Materials and Configuration. To meet the requirement of uniform irradiation of the chamber contents, spatially extended sources (fluorescent lamps) are distributed as uniformly as possible within a reflector about

Figure 3

SCHEMATIC DIAGRAM OF AIRFLOW CONTROL
AND MIXING SYSTEM OF SRI SMOG CHAMBER



*SELECTOR VALVES ARE SHOWN IN LOW-FLOW POSITION.

the exterior of the chamber. Chamber walls are transparent down to 300 nm. The major wall material is rolled sheets of $\frac{7}{32}$-inch Pyrex glass cut to form panels. Because access to the chamber interior is necessary for performing analyses and for evaluating eye irritation, one of the larger walls is constructed of panels of cast aluminum sheet. Another small panel of aluminum is used to support stirring pumps and inlet plumbing. The panels are mounted on a framework of special aluminum extrusions. These extrusions incorporate flanges and grooves for 6.4-mm silicone O-rings (baked under vacuum before use) to seal edges of panels, which are forced against the rings in the flanges by screwed-down exterior strips of aluminum cushioned by Neoprene.

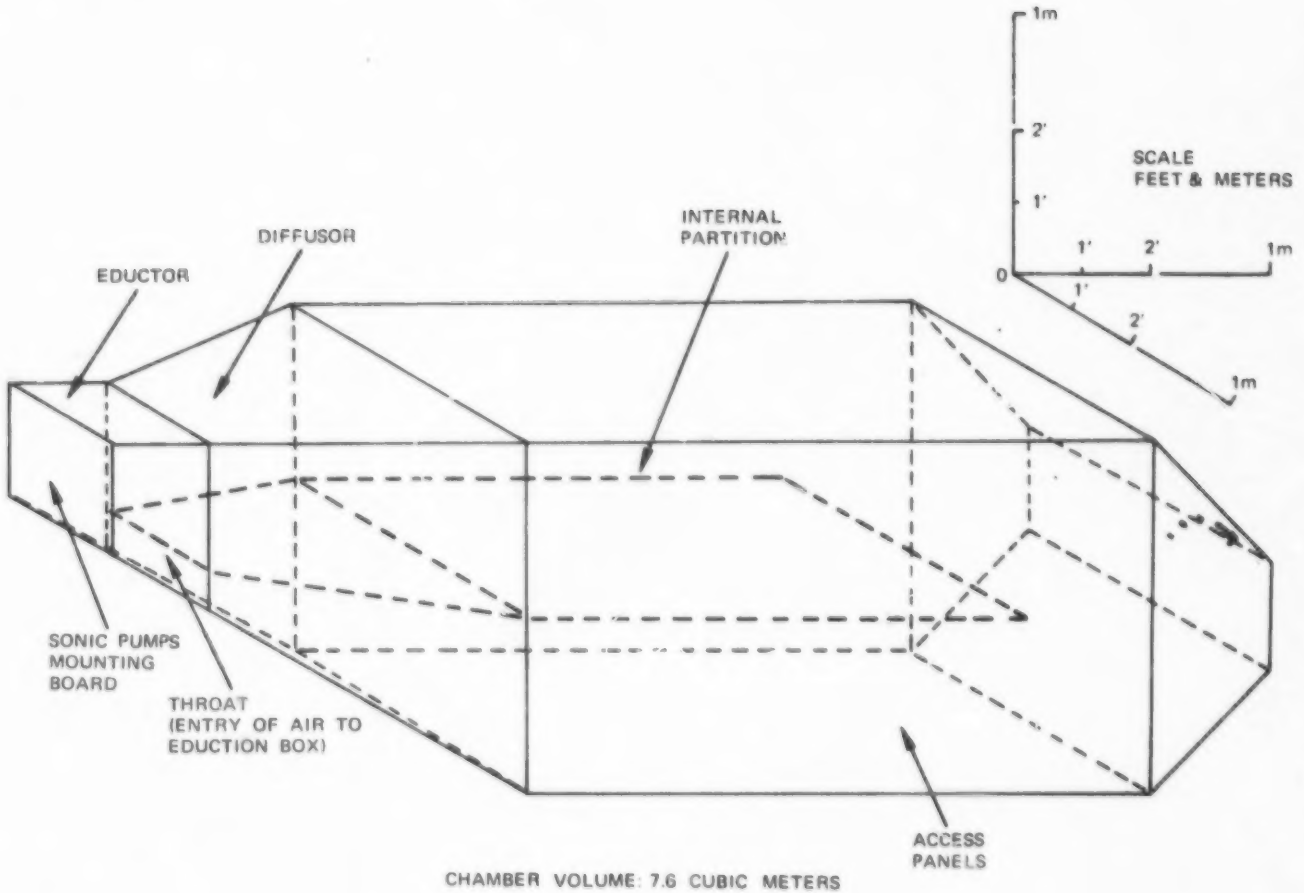
All interior surfaces are coated with Teflon, to reduce the accessibility of interior surfaces to acid-producing gases and to passivate them toward wall reactions, such as the decomposition of ozone. Aluminum surfaces are covered with a relatively heavy coating of Teflon, similar to that used on cooking utensils. Glass surfaces are coated with 0.02-mm transparent thermoplastic Teflon.

The use of sonic jet type pumps (Dauphinee, 1957) to circulate and stir the chamber contents avoids complications resulting from the use of impellers. Drivers are four 50-watt, 30.5-cm Permanent Magnet Speakers (Jensen) driven by 60-Hz voltage derived from the power line by way of variable autotransformers and step-down transformers. The speaker diaphragms are separated from the chamber contents by Teflon film cemented to the diaphragms. To lower the 60-Hz sound level, speaker pairs are phased in opposition. Use of this type of pump requires the use of an eductor-diffuser configuration because they are basically injector-type pumps.

The shape and dimensions of the chamber are dictated by a compromise among its various requirements, the type of stirring pump used, and the construction materials chosen. An additional chamber requirement, to reduce construction costs, is that it have minimum volume consistent with its use. The chamber dimensions and shape are shown isometrically in Figure 4. The elongated shape can accommodate a five-member eye irritation panel, members alternately standing and sitting along the aluminum access panels. A double-beam, long-path infrared spectrophotometer is also accommodated in this dimension of the chamber. The depth of the chamber is such that it accepts the optics of one of the spectrophotometer cells. The shapes of the chamber's ends are dictated by the airflow pattern within the chamber. Air flows from left to right at 5.7 m^3/min above the interior partition (see Figure 4) and then reverses direction and flows right to left below the partition to enter a converging channel leading to the inlet throat of the eduction box. The four jets of higher velocity mixture from the sonic pumps then entrain a larger mixture volume, which passes through an expanding diffuser to the space above the partition. The flow rate is great

Figure 4

ISOMETRIC SKETCH SHOWING SIZE AND
SHAPE OF SRI SMOG CHAMBER



CHAMBER VOLUME: 7.6 CUBIC METERS

enough to maintain mild turbulence, which is initiated at the sonic jets. In the stirred flow mode, the reaction mixture is injected into the mouth of the diffuser section of the flow channel.

Irradiation Source. It is fairly certain that radiation of wavelengths greater than 400 nm has little, if any, effect on the progress of the reactions in the case of trace concentration of nitric oxide and olefins in air. However, this chamber is being, and will be, used to study reactions of substituted olefins and nonolefinic organic compounds. Because the effect of long wavelength radiation is unknown for these compounds, it was decided to simulate approximately tropospheric radiation from 400 to 600 nm (46 kcal/einstein) and to simulate closely such radiation from 300 to 400 nm. Tropospheric radiation intensity is negligible below 300 nm. Because measured tropospheric radiation is widely variable, especially in the 300-400 nm region (U.S. Department of Health, Education, and Welfare, 1967), a realistic but somewhat arbitrary standard spectral distribution for simulation was selected.

Recent data available on spectral distribution include measurements made in the Los Angeles area in October 1965 (U.S. Department of Health, Education, and Welfare, 1967) and Leighton's estimates (Leighton, 1961, pp. 6-41). However, these two sets of data are not directly comparable. Leighton's considerations of path length in combination with contributions from sky and sun for the purpose of estimating the intensity directly concerned with photochemical absorption rates are equivalent to evaluating approximately the integral

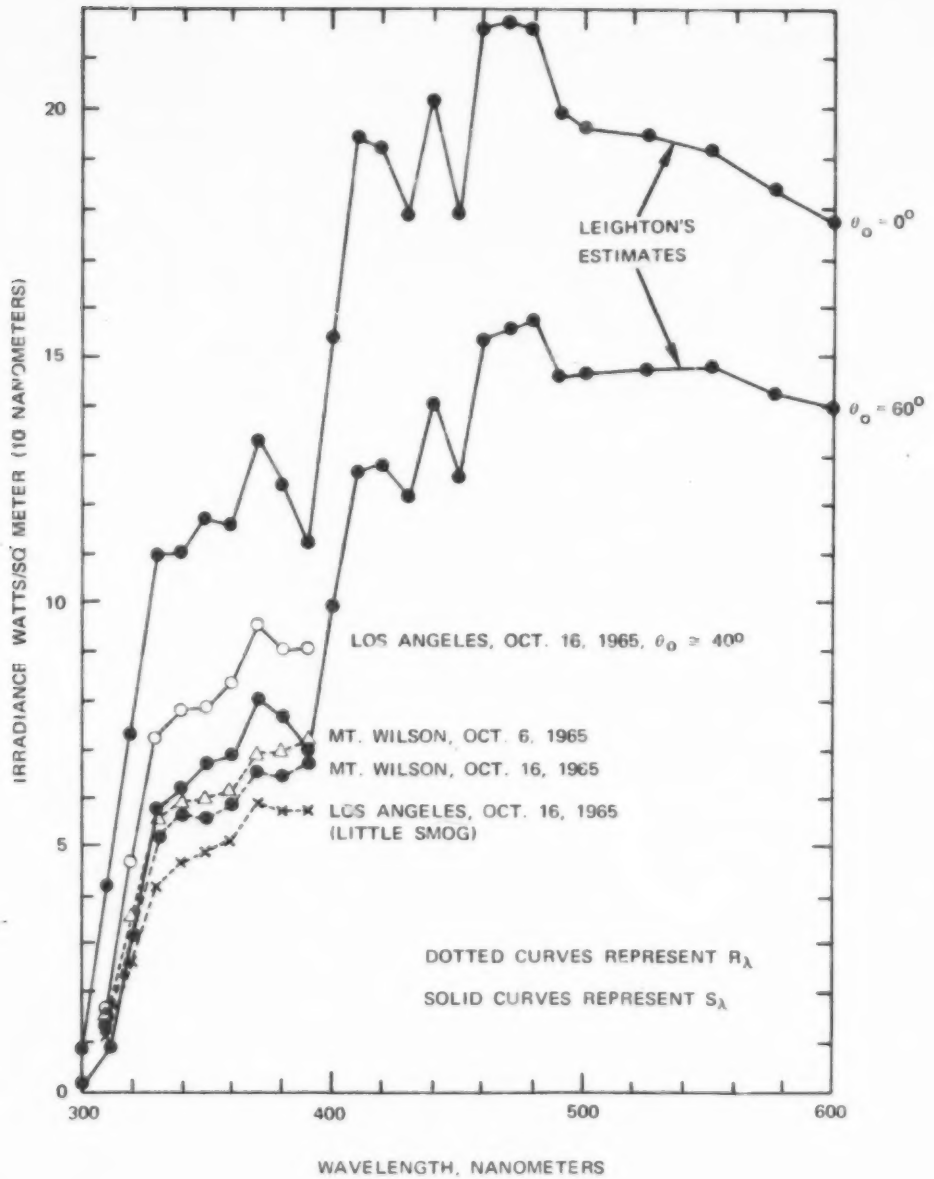
$$S_\lambda = \int_0^{2\pi} d\phi \int_0^{\pi} I_\lambda \sin\theta d\theta \qquad (3)$$

where I_λ is the specific intensity (Chandrasekhar, 1960) in watts/cm (10 nm) sterad at the spatial region of absorption and θ, ϕ are spherical coordinates centered at the region of absorption. Thus Leighton's J_λ, photons/sec cm^2 (10 nm), multiplied by appropriate wavelength dependent conversion factors, may be equated to S_λ; these converted values are plotted in Figure 5. The phototube and photocell measurements given by the U.S. Department of Health, Education, and Welfare (1967) evaluate the integral

$$R_\lambda = \int_0^{2\pi} d\phi \int_0^{\pi/2} I_\lambda d(\sin^2\phi) \qquad (4)$$

Figure 5

ESTIMATED AND MEASURED IRRADIANCE
FROM SUN PLUS SKY



If we neglect outgoing radiation, which is known to be small for the Los Angeles area at low altitudes and shorter wavelengths (Nader and Smith, 1967), and use Leighton's approximation of a uniformly bright sky, then these integrals may be expressed as

$$S_\lambda = \mathcal{I}_\lambda + B(\theta_o)$$

$$R_\lambda = \mathcal{I}_\lambda \cos\theta_o + \frac{B(\theta_o)}{2} \qquad (5)$$

where $\mathcal{I}_\lambda$ is atmosphere-attenuated direct solar intensity, θ_o = zenith angle of the sun, and as

$$B(\theta_o) = \int_o^{2\pi} I_{\lambda sky}\, d\phi \qquad (6)$$

where $I_{\lambda sky}$ is the specific intensity due to atmospheric scattering. Leighton's expression for J_λ implies

$$B(\theta_o) = \mathcal{I}_\lambda \frac{gi(1-T_{s\lambda})}{T_{s\lambda}} \cos\theta_o \qquad (7)$$

where, for his estimates of J_λ, he takes gi = 1 and uses the values for $T_{s\lambda}$ tabulated in his Table 4 (Leighton, 1961). Thus S_λ can be expressed approximately in terms of R_λ as

$$S_\lambda = \frac{2R_\lambda}{\dfrac{2\cos\theta_o - 1}{1 + \dfrac{gi(1-T_{s\lambda})}{T_{s\lambda}}\cos\theta_o} + 1} \qquad (8)$$

An average value of $\theta_o = 40^o$ was taken as applicable to diurnal maximum of the data obtained during the first two-thirds of October 1965 by Stair and Nader (1967); this value in combination with Leighton's table of values of $T_{s\lambda}$ allowed us to estimate values of S_λ on 16 October 1965 in Los Angeles. These estimated values are shown in Figure 5. Also shown in Figure 5 are three sets of data representing diurnal maxima of R_λ taken from the Stair and Nader data. Values calculated by R. J. Gordon (1967) from results of actinometry on 16 October 1965 (O-nitrobenzaldehyde) agree roughly from 300-400 nm with the integral under the S_λ curve for 16 October 1965.

The design objective for spectral intensity, S_λ, was chosen before the U.S. Department of Health, Education, and Welfare (1967) information was seen. The objective was to simulate Leighton's estimate of S_λ for $\theta_o = 0^o$ as closely as possible from 300-400 nm and to simulate it roughly from 400-600 nm. Data in Figure 5 show that this was about as good a choice as could have been made. The high maximum irradiance can be adjusted to lower values by selective extinguishing of lamps.

Calculating the number and types of fluorescent lamps required for a specific chamber's spectral irradiance can be no more than an approximation procedure (unless one wishes to be expensively elaborate) because of such unknowns as spectral reflectance of the reflector, variable absorption of commercial glass, and geometric factors. The following simplifying assumptions were made: (1) reflectance was sufficiently efficient to allow all radiation from a lamp to make one effective pass through the chamber; (2) glass attenuation was important in the short wavelength region only (at other wavelengths the transmission was assumed to be 90%); and (3) the spatial distribution of irradiance, S_λ, was uniform within the chamber. The quantity S_λ is related to the spectral energy density, U_λ (Chandrasekhar, 1960), within the chamber--that is, $U_\lambda = S_\lambda/c$, where c = velocity of light in m/sec. A steady-state equation can then be written for the energy balance:

$$\frac{dU_\lambda}{dt} = \frac{W_\lambda}{V} - \frac{c}{L} U_\lambda = 0 \qquad (9)$$

where W_λ = total spectral power of the lamps as attenuated by the walls, watts/10 nm; V = chamber volume, m^3; and L = some average transit length characteristic of the chamber geometry. This results in

$$W_\lambda = \frac{Vc}{L} U_\lambda = \frac{V}{L} S_\lambda \qquad (10)$$

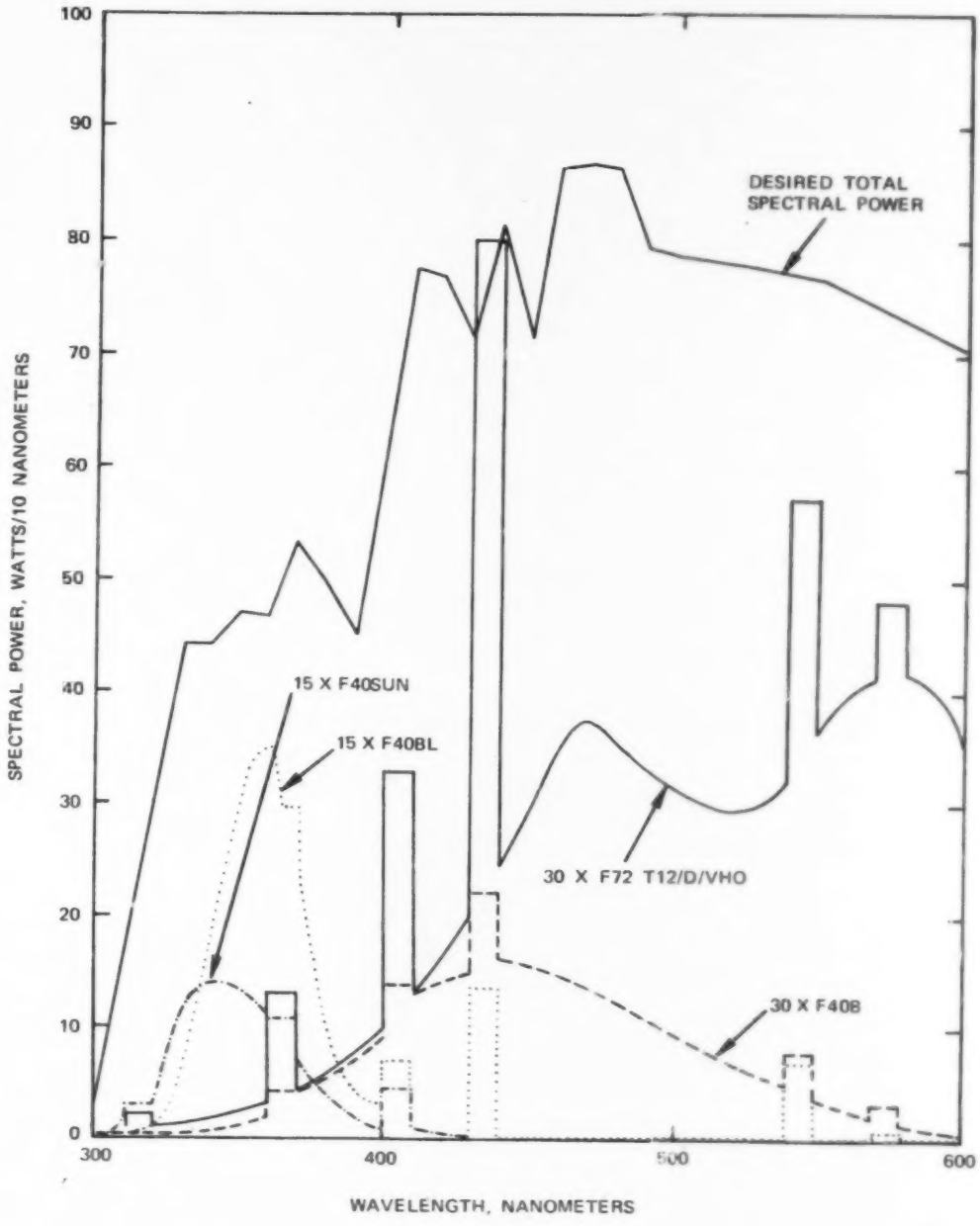
To estimate W_λ for a given chamber volume, a value must be assigned to L. This value will be roughly equal to the third root of the chamber volume if one dimension of the chamber is not much less than the others. For a 7.68-m^3 chamber of near cubical shape, one obtains $W_\lambda = 4\ S_\lambda$. Inspection of Figure 4 suggests a lower limit around 1.4 meters for L and an upper limit of 6 S_λ for W_λ. Because the estimating formula seemed likely to lead to an overestimate, the lower value of 4 S_λ was taken for calculating the first approximation to the lamp mix. On comparing the S_λ curve for $\theta_o = 0$ with spectral power distributions furnished by lamp manufacturers, a mix of Westinghouse sunlamp-type fluorescent lamps with blacklight, blue, and daylight fluorescent lamps came closest to fitting the S_λ curve. Because the most power would be furnished by the daylight lamps, the longest usable lamp with the highest power output commercially available--the 6-foot, VHO (very-high-output) daylight lamp--was chosen. The other lamps were chosen from among the lower power density, 4-foot, 40-watt lamps. Figure 6 shows the spectral power distribution of these lamps (as attenuated by 6 mm of Pyrex and multiplied by a factor given in the figure) compared with the desired spectral power curve. The estimated curve for the blue fluorescent lamps (F40B) is based on published relative spectral power curves, assuming conversion of 14.4 watts of 2537A radiation to emitted radiation for a 40-watt lamp, with a quantum efficiency of 0.9 and a power efficiency equal to the wavelength ratio. From data in Figure 6 it is obvious that the fit to the desired curve is not good near 300 nm because of severe attenuation through the chamber walls. Mercury lines also made it difficult to attain the desired curve. The best approach to a fit in the short wavelength region was to match the integral under the desired power curve from 300-400 nm, roughly matching the shape. In the long wavelength region, radiation would be furnished primarily by the blue and daylight lamps, and in this region the curve could be matched fairly closely except for excessive radiation at 405, 435, 545, and 575 nm. The calculation was further complicated by the lack of data on mercury lines at wavelengths longer than 405 nm for the sunlamps and by some interaction--via long wave phosphor absorption of shorter wavelength radiation and reemission of the energy within the phosphor's characteristic wavelength band--between long and short wavelength lamps.

Preliminary estimates of the number of lamps required led to the design of a reflector that will accommodate 72 VHO daylight lamps and 108 40-watt lamps. The initial composition of the lamp mixture and the final composition as modified by chemical actinometry considerations (see below) are given in Table 2.

Power for these lamps is furnished by a 220-volt, single-phase, 60-Hz, 3-wire power line. Ballast transformers for each type of lamp are symmetrically loaded on each side of this line. Thus, half of each lamp type is furnished with voltage 180^o out of phase relative to the other half. This, in combination

Figure 6

SPECTRAL POWER DISTRIBUTIONS OF VARIOUS
FLUORESCENT LAMPS ATTENUATED BY
6.35 MM OF PYREX COMPARED WITH DESIRED POWER CURVE



with the leading and lagging currents (respectively, relative to the voltage applied to a ballast) to each of the two lamps on a ballast, smoothes out temporal variations of light intensity. Ballasts are housed in a cabinet and are cooled by 34 m^3/min of ambient air, to avoid adding the power dissipated by the ballasts to the heat dissipated by the lamps.

Table 2

INITIAL AND FINAL LAMP MIXES

Type	Initial Mix		Final Mix	
	No.	Power (%)	No.	Power (%)
F72T12/D/VHO	72	72.6	72	72.6
F40B	30	7.6	30	7.6
F40BL	48	12.2	28	7.2
F40 sunlamps	30	7.6	50	12.6
Total watts	15,820		15,820	

Chamber Jacket. The chamber is enclosed within a rectangular jacket flush with the chamber access wall and the mounting panel for the sonic pumps. The minimum space between chamber and jacket is 15.2 cm; larger spacings occur near the ends of the chamber. These spaces are baffled to attain near uniform flow of cooling air around the chamber. Materials of construction are thin aluminum sheet and plywood riveted to a tubular frame.

The interior surface of the jacket serves as a mounting surface and reflector for the lamps. Originally it was painted with a high-reflectance white paint. Experience showed that an appreciable and useful increase of about 20% in light intensity in the short wavelength region could be obtained by lining the jacket with bright aluminum foil, and this is the present reflecting surface.

The jacket also serves as a duct for the cold air used to maintain chamber temperature. Air is furnished by an 85-m^3/min blower and by duct work that circulates air from an air-conditioner (21.1 kw [6-ton] rated capacity) through the jacket and returns it to the conditioner. A thermometer in the return air controls the output of the air-conditioning unit. Chamber temperature can be maintained as low as a constant 27°C with this system when all lights are on.

Analytical Facilities. The optics of one long-path cell of a double-beam infrared spectrophotometer (Perkin Elmer Model 221) are inserted into the chamber contents through a Teflon film diaphragm. The diaphragm is located in a port at one end of the access wall. The long-path cell was manufactured by Perkin Elmer according to the multireflection White Pattern; it is one meter long and is adjusted to obtain a folded path of 40 meters. The optical bench and len's mount of the cell are isolated from the chamber contents by Teflon films and Teflon coating. This spectrophotometer can measure sub part-per-million concentrations of compounds having strong absorption bands in spectral regions where water vapor and carbon dioxide do not absorb strongly.

Sampling ports with glass intake tubes were also built into the access wall. These allow sampling of the chamber contents for destructive analysis by the usual air pollution methods (Robert A. Taft Sanitary Engineering Center, 1965).

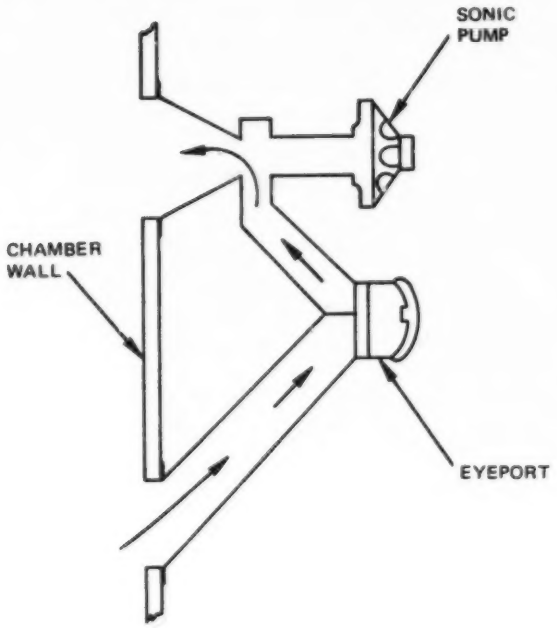
Eye Irritation Ports. A cross-section of one of the five eye ports along the chamber access wall is diagrammed in Figure 7. Each port is fitted with polyethylene welder's goggles. The eye ports are constructed of welded aluminum coated on inside surfaces with a black Teflon film. The protective glass and filters of the goggles were removed and the vents sealed. Silicone rubber sheet and foam (baked) is used to seal inlet and outlet flanges to the chamber access wall and to pad the goggles for fit to an individual subject's facial contours. This minimizes losses of the chamber contents and prevents inhalation of the reaction mixtures by the subject. The sonic pump drivers are 10-watt ceramic magnet speakers. The speaker diaphragm is isolated from the chamber contents by a slack Teflon film. Sixty-Hz voltage to the voice coil of the speakers is adjustable by means of a variable autotransformer and a step-down transformer.

The goggles are mounted in slides along with a polyethylene cover. A subject enters a booth, positions his head against the goggles, and slides the goggles over the port aperture, thus displacing the cover. At this instant he signals exposure start. Signaling is by means of a hand-held, push-button switch actuating the pen solenoid for one channel of a ten-channel event recorder. On experiencing perceptible irritation he signals again, thus generating a time interval characteristic of his response to the irritating qualities of the chamber contents. He then replaces the cover.

Two design objectives dictated eye port configuration: (1) to furnish in the neighborhood of a subject's eyes sufficient flux of chamber air so that transport of any irritant was not limited by depletion of irritant concentration in the neighborhood of the eye and (2) to make sure that no direct radiation from the fluorescent lamps impinged on a subject's eye.

Figure 7

CROSS-SECTION OF EYE PORT



These design objectives were met by use of short baffled conduits to and from the subjects' goggles in combination with a sonic pump to draw a stream of the chamber contents through the goggles and discharge it back into the chamber. Flow rate through the goggles must not be so large as to induce eye irritation by turbulent buffeting of the eyeball. On the other hand, it cannot be so low that mass transport of irritant to the eyeball is inhibited by depletion of the irritant in the neighborhood of the eyeball. In the limiting case that the eyeball serves as a perfect sink for irritant, the flux per unit eyeball area and per unit chamber concentration of irritant can be expressed in the form

$$\frac{J}{C_o} = \frac{Qf}{Af+Q} \qquad (11)$$

where j is flux per unit area, C_o is chamber irritant concentration, Q is volume flow rate through the goggles, f is a function of geometry and flow rate, and A is eyeball area. The function f has been evaluated for ideal geometric situations for flows ranging from laminar to turbulent (Bird, Stewart, et al., 1960; Levich, 1962).

Mildly turbulent flow, i.e., a Reynolds number of 2,000 or more, in combination with the sharp bends and transitions due to the baffling, was chosen as the regime within the goggles. This regime seemed a good compromise between facilitating mass transport by turbulence and avoiding irritating the eyes with excessive velocity. In addition, the linear velocity (around 2 mph) is typical of velocities encountered by pedestrians experiencing eye irritation on urban streets. Since the Prandtl number for air is small and the geometry is nonideal, values of the function f are uncertain (Levich, 1962). A rough estimate indicates a value of f around 0.3 to 0.4 cm/sec at Reynolds numbers below 10,000 for an idealized model of the situation inside the subjects' goggles. As the cross-sectional area is about 30 cm^2, the characteristic length about 4 cm, and eyeball area about 4 cm^2, we may write

$$\frac{j}{C_o} \sim \frac{0.3\, N_{Re}\, f}{f + 0.3 N_{Re}} \qquad (12)$$

For N_{Re} (Reynolds number) values of 2,000 to 10,000 this implies

$$\frac{j}{C_o} = f \sim 0.4 \text{ cm/sec} \qquad (13)$$

which is nearly independent of flow rate and is characteristic of the chamber concentrations of irritants. Incidentally, this implies that for an irritant concentration of 1 ppm, approximately 0.1 μg/min cm^2 can be deposited on the surface of the eye.

Facility Performance

Pure Air Supply. The purity of the air was tested by analytical means and by pure air irradiations in the chamber. Analysis for carbon monoxide showed none present (less than 0.5 ppm). Analysis for organic compounds, by injecting

a sample of the pure air supply into a flame ionization detector, suggested the presence of some organic material. Analysis for nitrogen oxides from the pure air supply just after construction of the apparatus showed a variable concentration around 0.05 ppm nitric oxide and 0.1 ppm nitrogen dioxide. After the pure air supply had been in operation a year, the nitrogen oxide concentration had stabilized at 0.1 to 0.3 ppm nitrogen dioxide with very little nitric oxide, with the exit temperature of the catalytic aftercooler at 600°K. This is roughly in accord with the equilibrium predictions shown in Figure 2.

Blank runs during which pure air was irradiated in the static mode for 8 hours yielded unmeasurable oxidant concentrations (less than 0.05 ppm) and little change in nitrogen oxide concentrations. No formaldehyde was detectable. Any organic impurity present in the purified air is apparently photochemically inactive.

Humidity tests of the pure air showed that water content remained within 35% ± 5% relative humidity at 25°C and 1 atm over an 8-hour period.

Reaction Chamber. Exchange rate with ambient atmosphere in the static mode was measured by following the concentration of inactive tracer compounds using the infrared spectrophotometer. A leakage rate of 1.5%/hr was derived from these data. This low figure is the result of fairly tight chamber construction in combination with good temperature control (which prevents "breathing" by the chamber).

The ozone half-life in the irradiated chamber is 6.7 hours. When corrected for exchange rate, this becomes 7.8 hours. This may be compared with the irradiated half-lives of 3.6 hours and 6 hours measured, respectively, in the 64- and 100-ft^3 chambers at the Bartlesville Petroleum Research Center (Dimitriades, 1967) and a value of 1.5 hours quoted by Levy and Miller (1968) for a chamber at Battelle Memorial Institute. The dark half-life for ozone is 17 hours, which becomes 20 hours when corrected for the exchange rate.

Light Intensity. Irradiance (S_λ) of the various types of lamps was measured by using a thermistor radiometer and by averaging over two 360° scans taken with the radiometer parallel to the xz and yz planes of an imaginary rectangular coordinate system at the point of measurement. The total, using a filter cut-off at 600 nm, was in approximate agreement with the design curve. However, the radiation below 400 nm was weak enough to allow a signal-to-noise ratio of around one, thus making radiometric measurements below 400 nm impossible with this instrument.

Typical Static Run. Figure 8 shows the progress of a typical static run in the chamber with initial concentrations of 1.0 ppm nitric oxide (plus a chamber background of 0.3 ppm nitrogen dioxide) and 8 ppm ethylene. These results are similar to those of other investigators (see, for example, Altshuller and Cohen, 1964). Differences can be plausibly explained by differences in concentration, temperature, humidity, spatial irradiance, reactor geometry and surface, and analytical error.

Discussion

The source of the organic contaminant in the pure air supply is unknown. Some methane may be surviving the catalytic oxidation, although this seems unlikely. A more likely source of contamination is the refrigerated distilled water used to rehumidify the purified air. Distilled water often contains appreciable dissolved, volatile, organic material. Although the concentration is less than the design objective of 0.5 ppm, the residual nitrogen oxides rich in nitrogen dioxide are the most serious impurity. An initially high dioxide concentration appreciably accelerates the initial course of static photooxidation of a nitric oxide - organic compound mixture with air, because the dioxide is the principal photoacceptor.

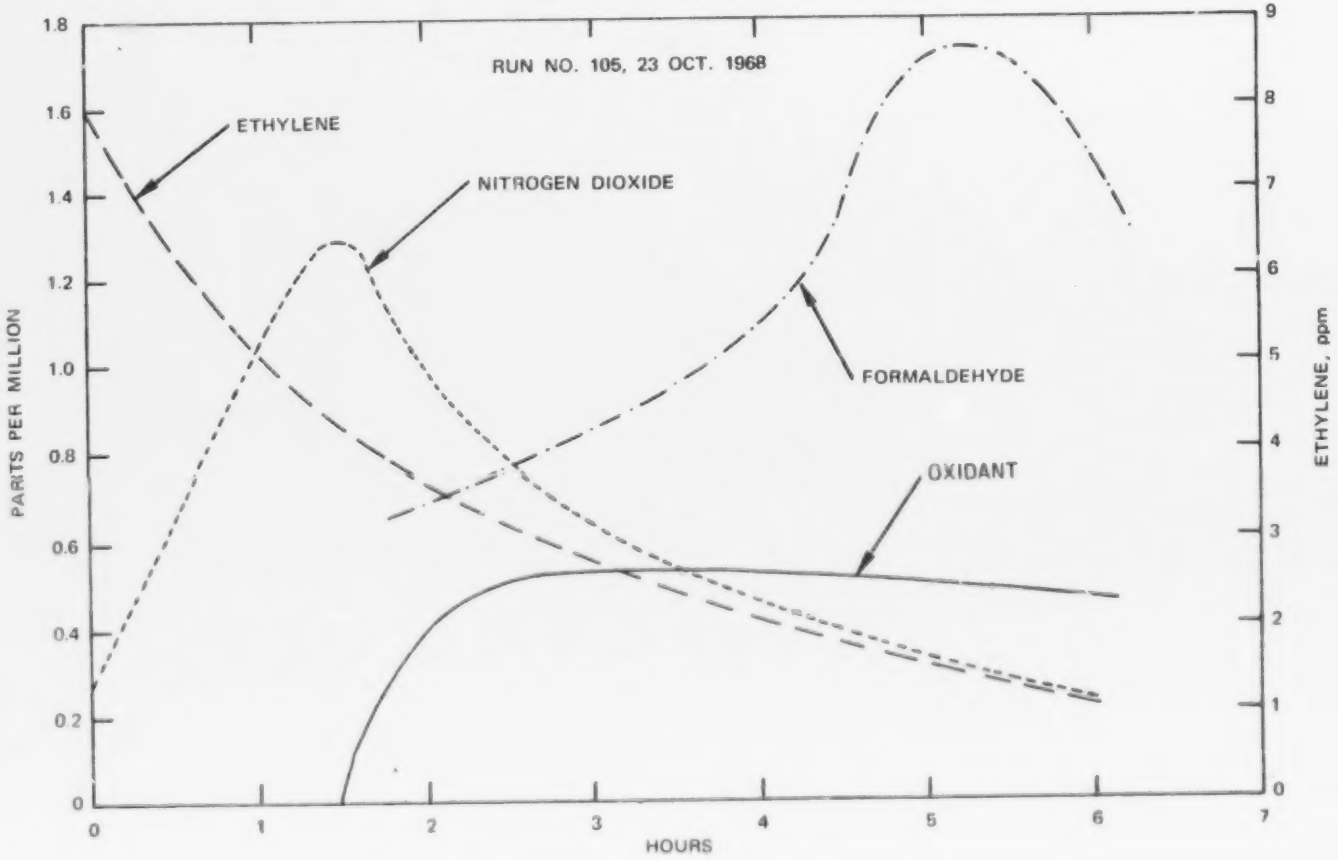
The spectral irradiance, although sufficiently representative of lower tropospheric irradiance to be satisfactory, is short of the goal in the short wavelength region by 15%. This could be corrected by replacing a few of the 72 VHO daylight lamps with six-foot blacklight lamps. The discussion of chamber performance above points up the disadvantages of fluorescent lamps as sources of radiation for this application. However, they have compensatory advantages, such as being highly efficient and being an extended source of radiation, which allows diffusion by simple means to obtain a nearly uniform spatial distribution of irradiance. Fluorescent lamps are also inexpensive and require inexpensive auxiliaries. A closer approximation to sunlight could be obtained by using sources such as incandescent tungsten filaments stabilized by halogen in quartz bulbs, xenon arcs, or carbon arcs. However, the heat disposal and radiation filtering arrangements would become relatively elaborate, and diffusion of the radiation would require some care and expenditure.

The facility described here is being used for a study of the photoreactivity potential of trichloroethylene. On completion of the current program, other studies will be undertaken. Studies being considered concern development of a realistic methodology of evaluating the photochemical smog contributions of certain industrial emissions and elucidating some aspects of the kinetic mechanism of photochemical reactions in the polluted troposphere.

Building of chamber sponsored by the member companies of the Manufacturing Chemists' Association Ad Hoc Task Group on Photoreactivity of Trichloroethylene, Washington, D.C.; research with chamber sponsored by Manufacturing Chemists' Association.

Figure 8

STATIC RUN WITH INITIAL CONCENTRATIONS OF 1.0 PPM NITRIC OXIDE AND 8 PPM ETHYLENE IN SRI SMOG CHAMBER



LITERATURE CITED

Altshuller, A. P., and Cohen, I. R., Intern. J. Air Water Pollution, 8, 661-632 (1964)

Bird, R. B., Steward, W. E., and Lightfoot, E. N., Transport Phenomena, Wiley, New York, 1960

Brunelle, M. F., Dickenson, J. E., and Hamming, W. J., "Effectiveness of Organic Solvents in Photochemical Smog Formation," Air Pollution Control District of the County of Los Angeles Report, July 1966, pp. 52-76

Bufalini, J. J., and Altshuller, A. P., Air and Water Pollution, 7 (8), 769-771 (1963)

Chandrasekhar, S., Radiative Transfer, Dover, New York, 1960, pp. 1-5

Dauphinee, T. M., Rev. Sci. Instr., 28 (6), 452 (1957)

Dimitriades, B., J. Air Pollution Control Assoc., 17 (7), 460-466 (1967)

Gordon, R. J., "Photochemical Measurements," in Pilot Study of Ultraviolet Radiation in Los Angeles, ed. by J. S. Nader, Public Health Service Publication No. 999-AP-38, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1967, pp. 37-47

Haagen-Smit, A. J., Bradley, C. E., and Fox, M. M., "Formation of Ozone in Los Angeles Smog," Proc. of Second National Air Pollution Symposium, May 5-6, 1952, Pasadena, Calif., pp. 54-56

Hamming, W. J., and Lausche, R. G., "Effect of Emissions of Organic Solvents on Los Angeles Photochemical Smog," Proc. Third Technical Meeting, West Coast Section of the Air Pollution Control Assoc., Monterey, Calif., Sept. 26-27, 1963, pp. 153-184

Jones, R. H., "Kinetics and Catalyst Selection in the Combustion of Atmospheric Trace Contaminants," in "Aerospace Life Support," Chem. Eng. Progr., Symposium Series, 62 (No. 63), 81-88 (1966)

Leighton, P. A., Photochemistry of Air Pollution, Academic Press, New York, 1961

Levich, V. G., Physicochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, New Jersey, 1962

Levy, A., and Miller, S. E., "The Role of Solvents in Photochemical Smog," paper presented at the 61st Annual Meeting of the Air Pollution Control Assoc., St. Paul, Minn., June 23-27, 1968

Lewis, G. N., and Randall, M., Thermodynamics, as revised by K. S. Pitzer and L. Brewer, McGraw, New York, 1961, pp. 669-689

McAdams, W. H., Heat Transmission by Conduction and Convection, Chemical Engineers Handbook, 3rd ed., McGraw, New York, 1950, p. 469

Nader, J. S., and Smith, C. F., "Filter Photocell Measurements," in Pilot Study of Ultraviolet Radiation in Los Angeles, ed. by J. S. Nader, Public Health Service Publication No. 999-AP-38, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1967, pp. 5-20

Noyes, R. M., as quoted by S. W. Benson in The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960, pp. 451-452

Nusselt, Z., Ver. deut. Ing., 53, 1750, 1808 (1909)

Robert A. Taft Sanitary Engineering Center, "Selected Methods for the Measurements of Air Pollutants," U.S. Public Health Service, Information Bulletin No. 999-AP-11, Cincinnati, Ohio, May 1965

Schuck, E. A., "Eye Irritation from Irradiated Auto Exhaust," Report No. 18, Air Pollution Foundation, Los Angeles, Calif., March 1957

Stair, R., and Nader, J. S., "Filter-Phototube Measurements," in Pilot Study of Ultraviolet Radiation in Los Angeles, ed. by J. S. Nader, Public Service Publication No. 999-AP-38, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1967, pp. 21-36

U.S. Department of Health, Education, and Welfare, Pilot Study of Ultraviolet Radiation in Los Angeles, ed. by J. S. Nader, Public Health Service Publication No. 999-AP-38, Cincinnati, Ohio, 1967